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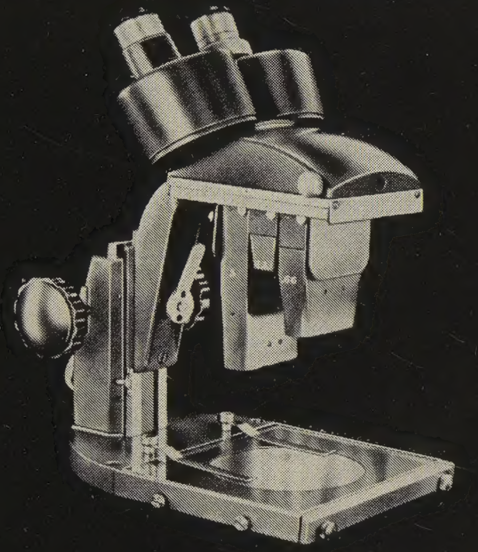

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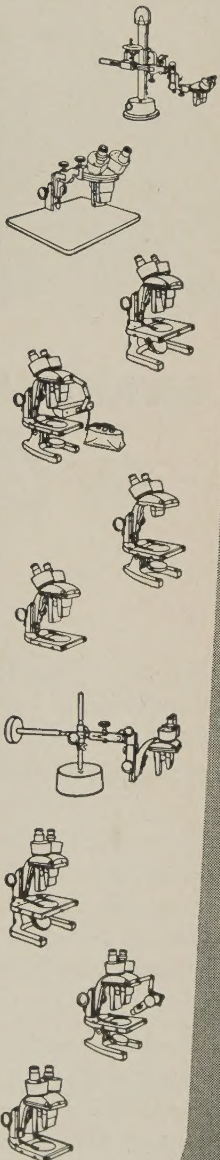

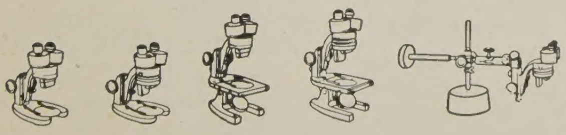

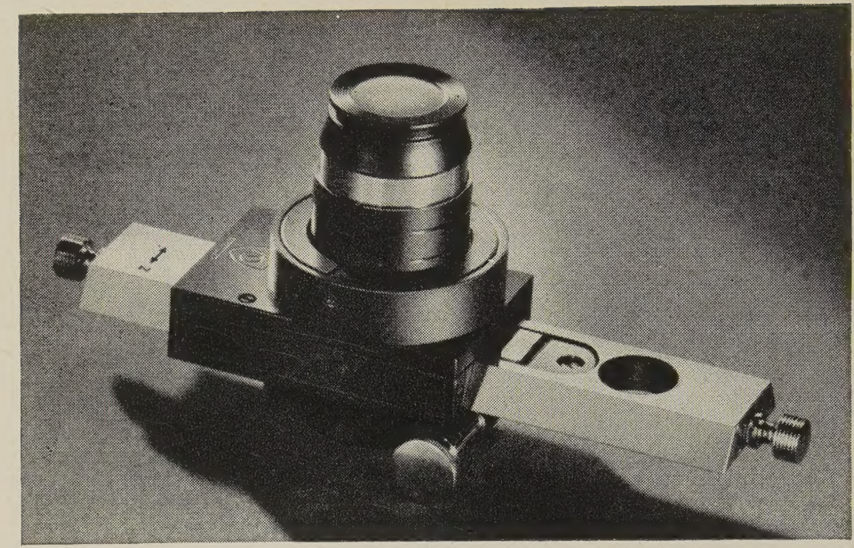

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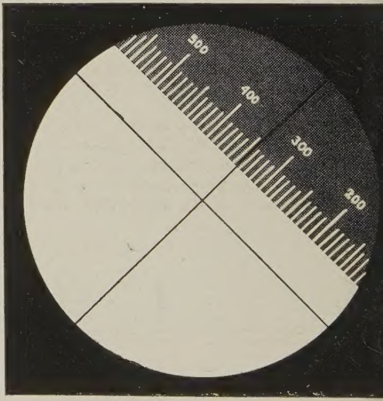

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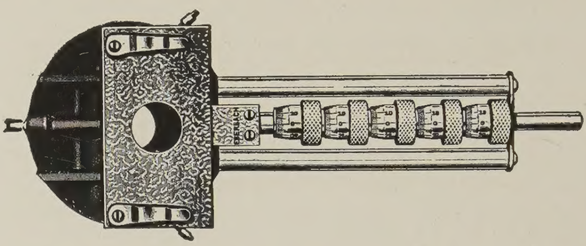

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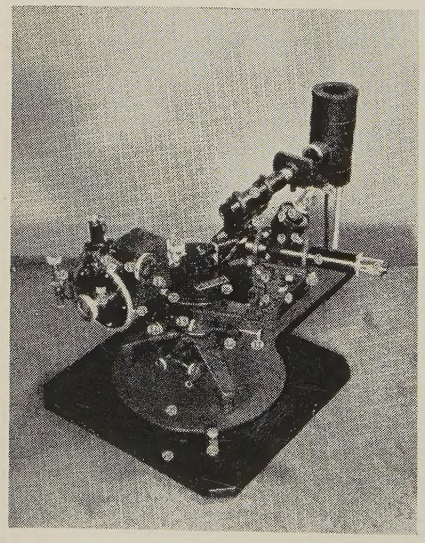

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A SIMPLE POINT COUNTER FOR THIN-SECTION ANALYSIS

F. CHAYES, *Geophysical Laboratory, Washington, D. C.*

ABSTRACT

A manually operated point counter for thin section analysis is described. The machine is sturdy, inexpensive, and easily operated. Its precision has been tested by analyzing 47 thin sections in duplicate and computing the analytical error, or standard deviation of a single analysis, from the observed variance of the differences. The error distribution is effectively binomial and the precision of the instrument is somewhat better than that of the Wentworth-Hunt and Hurlbut integrators. Average operating speed is about four times that of the Wentworth-Hunt and twice that of the Hurlbut machine.

INTRODUCTION

Estimates of modal composition have always been of central importance in petrography, and the various instruments and techniques designed to provide them are too well known to require review here. It seems, however, to have escaped notice that the theoretical underpinning of modal analysis has changed at least four times; thin section analyses are still called "Rosiwal analyses," though it is almost safe to say that no microscopist has made a Rosiwal analysis since the introduction of the Shand micrometer in 1916.

In the method of Delesse as modified by Sollas the individual sample was an entire microscopic field, and the items in this sample were the areas of grains or portions of grains contained in the field. In the Rosiwal method the sample consisted of a number of parallel lines so spaced that no two cut the same grain; the items in the sample were the distances marked out by the intercepts of grain boundaries on these lines. In Shand's procedure the condition that no grain be cut by more than one line is abandoned,* and the lines, or traverses, are distributed evenly over the surface of the specimen regardless of grain size. The importance of this change is two-fold: it permits much greater precision in the estimate of the composition of a given specimen, and it both permits and requires a sharp distinction between the reproducibility of a single analysis on the one hand, and differences between thin sections on the other.

---

* On rereading the original description of the Shand stage I find it specifies that no grain be cut by more than one traverse. Formal abandonment of this condition is apparently due to Wentworth (*Jour. Geol.*, 1923).

The basic sampling design of the Shand stage is carried over intact in the Wentworth-Hunt, Dollar, Leitz, and Hurlbut instruments, all of which have the advantage that several constituents may be estimated simultaneously. This sampling design is identical with the well known "trapezoid rule" for graphical integration (1, p. 272).

A new basis for thin section analysis was introduced by Glagolev (2, 3) in 1933. In Glagolev's procedure the regular spacing between traverses is retained, but the traverse itself is broken into a series of equally spaced points. The operator identifies the material under the cross-hair intersection and depresses the appropriate key of a tabulating device; the depression of any key on the tabulator triggers a mechanism which translates the stage a fixed distance along the line of traverse. This procedure is repeated until the proper distance has been traversed, the stage is reset and a new line run, and so forth. The sample is thus a bilaterally symmetrical (but not necessarily isotropic) grid of points.

In the course of the last few months I have made nearly 300 thin section analyses with a hand operated version of Glagolev's device. The instrument has proved superior in several respects to any machine now on the market. It is sturdy, inexpensive, and easily assembled from stock parts. It has about the same advantage in time over the Hurlbut instrument as the latter has over the Wentworth; an hour's work on the Wentworth will usually take about a half-hour on the Hurlbut and fifteen minutes on the point counter. The tabulator dials are set at zero at the start of each analysis and are read only once, at the end of the analysis; with a slide rule the number frequencies are easily converted to percentages in two or three minutes. Whereas other instruments can handle only a fixed number of constituents simultaneously, additional counters may be added to the tabulating unit of the point counter at will. The instrument may be used on much finer grained material than can be handled with the Hurlbut integrator and its precision is somewhat superior to that of the Hurlbut and Wentworth instruments.

THE POINT COUNTER

A standard Spencer or Bausch and Lomb mechanical stage is easily adapted for point counting. The knurled nut at one end of the horizontal thread is replaced by a click wheel of the type shown at *A* in Fig. 1; in my instrument the notches are spaced on the wheel so that the distance between centers is equivalent to a horizontal traverse of 0.3 mm. A spring stop is mounted on the frame of the stage and adjusted so that each translation of 0.3 mm. is signalled to the operator by an easily audible click. A similar arrangement on the rack and pinion which controls the "vertical" motion of the stage insures equal spacing of the traverse lines;† this wheel is calibrated so that each translation is 0.5 mm. and I have so far systematically spaced the traverses at 1 mm.—or two clicks—apart. Using a standard area of 1 inch by $\frac{3}{4}$ inch this means that each analysis consists of about 1400 points spaced at 0.3 mm. in one direction and 1 mm. in the other. Holes in the slide are ignored, but if there are many of these there is no point in running the analysis. The outline of the area to be analyzed is traced onto the thin section from a template, in India ink; some irregularity in the number of points is introduced by inaccurate tracing.

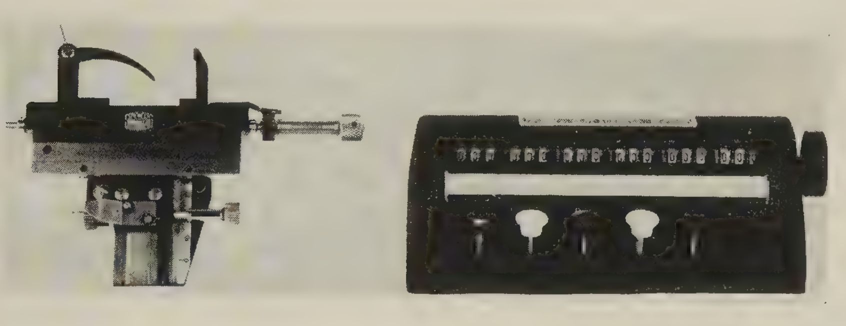

FIG. 1. Point Counter (A) and Tabulating Unit (B)

The tabulator at present consists of a five-unit Clay-Adams blood cell counter (*B* in Fig. 1). This is an extremely convenient instrument, but will record only five constituents. A similar and somewhat cheaper six-unit tabulator is made by the Denominator Corporation, but the keys on this are rather widely spaced. Where more than five constituents are to be recorded, a complete block of the same type or separate Veeder counters may be added.

Greater precision may be obtained by reducing the vertical traversing interval as well as by inserting additional horizontal cross hairs in the ocular. With two of these and a vertical interval of 0.5 mm. 8400 counts could be obtained from the standard $\frac{3}{4}$ inch × 1 inch area used in the tests described below. This would more than double the time required for analysis and it would require four- instead of three-digit counters. These can be purchased separately but are not available in blocks.

PRECISION OF THE POINT COUNTER

Under proper circumstances precision is best determined by making replicate analyses on the same sample. Where there is doubt about the independence of the replications, however, this procedure may give rise to unwarranted optimism about the precision of the measurement.

---

† Mr. F. A. Rowe, who installed the click wheels on the stage shown in Fig. 1, informs me that his work required about 6 hours.

For some time I have felt that my study of the precision of the Hurlbut integrator (1) was open to question on this score. In that study traverses spaced at 0.1 mm. were made over the surface of a thin section and recorded separately on numbered cards. The cards were then assembled in ten sets, the first consisting of traverse numbers 0, 10, 20, . . . , the second of 1, 11, 21, . . . , and so forth, each set being regarded as a separate analysis made at a traverse interval of 1 mm. This gave a group of ten analyses from which standard deviations were computed for each of five constituents. Now the 0.1 mm. spacing of the original traverses was very small in relation to the grain of the rock, so it is reasonable to suppose that in general adjacent traverses would be more similar to each other than distant ones. Thus the initial traverses of each synthetic analysis, numbers 0, 1, 2, . . . , would be more similar than if they had been chosen randomly from the entire array; this would be true also of the second traverses, 10, 11, 12, . . . , and so forth for the entire set.* The effect of positive correlation between adjacent runs would be to reduce dispersion of the synthetic analyses. Even by this rather elaborate *tour de force* only ten replications were obtained and these were combined with similar computations made from the same data for synthetic analyses with traverse intervals of 0.9 and 1.1 mm.; for this reason too it would be likely that the observed value would somewhat underestimate the true dispersion.

For the present test a different procedure was adopted. In the machine as described above there are two possible settings of the thin section. Each of 47 thin sections (of the Milford, N. H., Westerly, R. I., and Barre Vt., granites) was analyzed twice. The entire suite was first run with the label of each slide at the left side and then with the slide rotated 180°; the test was spread out over three weeks and the replications were made under varying conditions of illumination, operator fatigue, and pressure for time. Only virtually perfect thin sections were used, so that variations introduced by ignoring or "identifying" holes in the thin sections are not included in the result. Except for this, however, the conditions of the test are very like those encountered in daily routine.†

The testing procedure yields a series of 47 paired differences for each constituent. The variance of any set of differences is the mean of the squared deviations, or

---

* Unfortunately the record of the original traverses has gone the way of all scrap paper, so it is no longer possible to determine whether this was in fact the case.

† In my own work I have found it best to refrain from analyzing slides of inferior quality. There is always a strong temptation to use results obtained from such slides if they are not discordant and to discard them if they are. Under such circumstances there is little point in making the analysis.

$$s_d^2 = \frac{1}{n} \mathop{S}_{i=1}^{n} (X_i - \mu) \qquad (1)$$

and since μ is by definition zero (each pair of analyses being run on the same slide) equation (1) may be written

$$s_d^2 = \frac{1}{n} \mathop{S}_{i=1}^{n} (X_i)^2. \qquad (2)$$

From the design of the experiment the variance of a difference is the sum of two independent variances which are equal to each other and to the square of the precision error—e.g., the "precision variance"—of a single analysis, or

$$s_d^2 = 2s_a^2 \qquad (3)$$

so that, finally, the precision error is given by

$$s_a = \sqrt{s_d^2/2} \qquad (4)$$

where s_d^2 is computed from the data according to equation (2). Results of the test are shown in Table 1.

TABLE 1. DUPLICATE ANALYSES OF 47 THIN SECTIONS OF GRANITE

Mineral	Mean $\bar{x}$	Standard Deviation s_x	Variance of Differences s_d^2	Precision Error of a Single Analysis s_a
Feldspar+Musc.	65.84	3.77	2.98	1.22
Quartz	26.45	2.75	1.46	0.85
Biotite	6.65	2.82	0.63	0.56
Others	1.06	0.42	0.22	0.33

The precision error given in column 4 of Table 1, and as used throughout this paper, is a standard deviation. On the assumption that the error distribution is normal there is a two to one chance that a single analysis will not differ from the "true value" by more than this standard deviation, the "true value" being defined simply as the mean of a great many analyses of the same slide. Similarly, the probability of a difference between "true" and observed values as large as $2s_d$ is no more than 5%. By the method used to reach Table 1, however, no slide is analyzed more than twice, so that "true" values are not available for comparison.

The reason for defining precision error in terms of dispersion about the "true value" is just that in every day work we usually regard the observed as an estimate of the "true"; it is essential therefore to be able to specify, with known probability, the range in which the "true value" may lie.

The tests to which the instrument is likely to be subjected will probably be on a pretty small scale, and where pairs of values are compared, whether obtained by one operator or two, the proper index of dispersion to be applied to the differences is the square root of the appropriate entry in column 3 of Table 1. It is important to realize that theoretically *no* difference is too large to occur, and that in a large enough sample about a third of the differences should be larger than s_d. For example, of the 47 biotite differences obtained in this test, 31 are less than s_d for biotite, which is 0.795, 13 lie in the range $s_d \leq d \leq 2s_d$, and 3 are larger than $2s_d$; the largest is 2.3, or nearly three times s_d. Distributions of differences for the other constituents are comparable.

Although the selection of points in a single analysis is not random in the usual sense, for the entire array may be regarded as fixed once the initial point is chosen, it may be shown that the results in Table 1 conform rather nicely with what would be expected if the sampling were truly random. In a perfectly adjusted machine of the type pictured in Fig. 1, a thin section area $\frac{3}{4}$ inch ×1 inch offers a total of 2800 points of which 1400 are used for any single analysis. If the points forming each analysis were randomly chosen the case would conform exactly to hypergeometric sampling, in which a sample of fixed size is drawn, without replacement, from a lot containing a finite number of items. The standard deviation for sampling of this type is given by

$$s_h = \sqrt{n \cdot \frac{M}{N} \cdot \frac{N-M}{N} \cdot \frac{N-n}{N-1}} \qquad (5)$$

where n = number of items in the sample.
N = number of items in the lot.
M = number of items of one particular kind in the lot.

If knowledge about the lot is lacking, as will usually be true, the fractions M/N and $(N-M)/N$ are estimated from the sample. As N increases, the term $N-n/N-1$ approaches unity and in the limit as $N \rightarrow \infty$ equation (5) reverts to the common binomial form

$$s_b = \sqrt{npq.} \qquad (6)$$

If $N=2n$ the variance will be approximately half and the standard deviation a little over 70% of the binomial parameters. If $N=4n$ the hypergeometric standard deviation is 86%, and if $N=10n$ it rises to 95%, of the binomial parameter. For both N and n large the advantage of hypergeometric sampling is rapidly lost with increase in the ratio N/n.

In a perfectly adjusted machine the sampling would be truly hypergeometric, with N = 2n. As the machine wore, end play would increase in the thread, the notches on the clicking wheels would enlarge and the tension of the springs would decrease. All of these changes tend to increase the number of possible points (the lot size, N), and an increase in the speed of operation would have the same effect.

We should expect then that if the sampling were effectively random, estimates of analytical error would be conformable with parent standard deviations intermediate in size between the simple binomial and the hypergeometric with N = 2n. This in fact proves to be the case. The average number of points per thin section was 1391. Using the mean values of Table 2 as estimates of p, and M/N, and taking n = 1391, N = 2800, equations 5 and 6 may be solved to yield theoretical estimates of precision error comparable to the observed values shown in Table 1. Equations 5 and 6 give the error as a number of points; in Table 2 the results are shown on a percentage basis (100s/1391).

TABLE 2. COMPARISON OF THEORETICAL AND OBSERVED ANALYTICAL ERROR

Mineral	Mean	Error of a Single Analysis as % of the whole		
		Hypergeometric	Observed	Binomial
Feldspar+Musc.	65.84	0.90	1.22	1.27
Quartz	26.45	0.84	0.85	1.19
Biotite	6.65	0.47	0.56	0.67
Others	1.06	0.20	0.33	0.27

The chief use of the error estimates of Table 2 is in judging single analyses. With the procedure described above, the least count of the instrument is 1/1400 so that an analysis should not be reported beyond tenths of a per cent. To this degree of approximation $s_h \leq s_{obs} \leq s_b$, as may be seen by rounding off the error entries of Table 2 to the first decimal.

For practical purposes the analytical error may be regarded as binomial. Over a short period of time results obtained from a single instrument may benefit by the hypergeometric character of the sampling. But if the machine is constantly used and the replications are made at long intervals the error distribution will probably be effectively binomial. This will almost certainly be so if the same slide is analyzed on a number of different instruments, and in any case the difference is small. For the curious fact that a clearly non-random sampling procedure behaves as if it were random I have no satisfactory explanation. In these thin sections the average grain diameter is several times the distance between points, so that adjacent points are certainly not independent. But there is no connection between the locations of grain boundaries and the selection of points. It may be that the randomness operates in terms of clusters or runs of points.

CONCLUDING REMARKS

Enthusiasm at finding a simple and relatively rapid method for analyzing thin sections has led me to make rather generous claims for the instrument described in this note. By way of conclusion I should like to offer evidence substantiating these claims, to anticipate a few criticisms, and to give an example or two illustrating the utility of the instrument.

It has already been suggested that in the only similar precision test of the Hurlbut integrator (1) the testing procedure is not entirely comparable with that used here. Both tests, however, were attempts to estimate the same error; both being run on granite, each offers estimates of precision error at about the same composition levels. The results are compared in Table 3 below.

TABLE 3. COMPARISON OF PRECISION TESTS FOR HURLBUT INTEGRATOR AND POINT COUNTER

Composition Level	Hurlbut Integrator*			Point Counter†		
	$\bar{x}$	Prec. Error	$\frac{\text{Prec. Error}}{(2n)^{1/2}}$	$\bar{x}$	Prec. Error	$\frac{\text{Prec. Error}}{(2n)^{1/2}}$
Principal						
Feldspar	61.0	1.93	0.35	65.8	1.22	0.18
Quartz	29.6	1.08	0.20	26.4	0.85	0.12
Minor	7.8	0.94	0.17	6.6	0.56	0.08
Accessory	1.6	0.47	0.09	1.1	0.33	0.05

* Data from Table 6 of reference 1.

† Data from Table 1, this paper.

For normal distributions σ itself is normally distributed with standard deviation $\sigma_\sigma = \sigma/\sqrt{2n}$; each entry in columns 3 and 6 of Table 3 is an estimate of the error contained in the value immediately to the left. In each case the estimated precision error of the point counter is less than that of the Hurlbut integrator and in three of the four comparisons the difference is greater than the sum of the estimated σ_σ values.

A more refined test of Table 3 would be to use the observed difference at any level divided by either σ_σ estimate at that level as a normal deviate, on the assumption that the true difference is zero. Still another would be to compute the standard deviation of each difference on the assumption that the samples were *not* drawn from the same population.

Both these tests, as well as the simple comparison suggested in the preceding paragraph assume that the error distribution is "sufficiently normal," but there seems little reason to doubt this except possibly at the "accessory" composition level. All three procedures lead to about the same result: the point counter is certainly as precise as the Hurlbut integrator and probably a little more so.

No comparably detailed direct test of the Wentworth-Hunt instrument seems to have been made. My own work (1) suggests that if the traverses are evenly spaced—something which could not be accomplished without slightly modifying pre-war models—it has about the same reproducibility as the Hurlbut, except at the "accessory" level, where it seems a little better. (Strictly the test showed only that there was no necessity to assume any difference between the precision of the two instruments.)

The sampling design of all instruments which attempt to measure a continuous line is theoretically superior to that of the point counter. Their difficulty is in practice not theory. Manually operated instruments of this type require a reading (and recording) of each dial at the end of each traverse; each reading contains an error and though these errors *tend* to balance out, in general they will not exactly compensate in the course of a single analysis. Errors made by the eye in using the manually operated machines are made by the hand in operating the Hurlbut stage; almost invariably one over- or under-runs grain contacts. A Hurlbut stage which would operate at high speed without over- or under-running would no doubt be considerably superior to the point counter described in this note; in effect it would be a point counter counting a very large number of points.

While the possibility of errors in identification can never be entirely excluded, it should always be held to a minimum in any work of this type. To get results of the necessary quality and quantity it is desirable to work at high speed; minerals which cannot be instantaneously, or almost instantaneously, distinguished from each other should not be separately recorded. Identification errors will be erratic, highly subjective, and, in practical terms, virtually unmeasurable. Only an operator whose bravery exceeds his wisdom will attempt analyses when he has reason to suspect that errors of identification will be more than a trifling component of the total precision error.

Finally, there is the question of the speed at which analyses can and should be run. This will no doubt vary with the ability and experience of the operator, but I believe that the relative rates at which the point counter, the Hurlbut integrator, and the Wentworth-Hunt stage are conveniently operated will be about as stated in the abstract. My experience with the point counter suggests that a rate of between 75 and 100 counts per minute is not at all excessive after a little practice; this is an over-all figure and includes delays for identification, change of focus, movement of the vertical traverse knob, etc. It can be maintained without difficulty for the 15 to 20 minutes required for an analysis. These figures are based largely on work with fine grained granites, 7 constituents being recorded in each analysis. Although the tabulation of additional constituents is at first very troublesome, I believe anyone who has even a passing acquaintance with touch-typing will find that after a little practice—and a few worthless analyses—the number of constituents separately recorded has no appreciable effect on the rate of operation. Grain size is a critical factor in determining the rate of operation, since if the grains are small the runs of identical points will all be short. Very fine grained rocks cannot be done at all, but it is my impression that the point counter allows more leeway in this direction than any of the continuous-line recorders.

Prolonged use of any of the instruments mentioned in this note leads to fatigue and unreliable results. It is always best to take a five or ten minute break between analyses, and I have so far never spent a full day analyzing thin sections. A half-dozen analyses represents a pretty fair morning's work.

It is virtually certain that a long analysis done slowly will be better than a short one done quickly, but it is not at all sure that the increased precision will be either very large or very useful. Quantitative modal analysis has fallen so far behind interpretive petrology that rather severe measures are in order; in the present status of our subject many good analyses are worth more than a few excellent ones. For practical purposes we need require only that the precision error of a single analysis be small in relation to the expected differences between rocks. In many experimental designs the precision error, if it is known, can be extracted from the total variance. In many others the hypothesis being tested is so general that the operation of extracting the precision error from the total variance is scarcely worthwhile.

This particular point is much more readily made by illustration than by argument. A deep lavender fluorite, occurring in very small grains, is the most conspicuous accessory constituent of the Westerly, R. I., granite. The mineral is present in every one of 24 specimens, each specimen coming from a separate quarry and the quarries being anywhere from a hundred yards to over ten miles distant from each other. Yet in 24 analyses, of about 1400 counts each, not a single grain of fluorite happened to fall at the cross-hair intersection. Proper analysis for such a minor constituent would require a very extended, time-consuming count. For a first approximation it seems to me far more useful to know that each of 24 samples yielded less than 0.1% fluorite than it would be to know that each of 6 samples yielded fluorite in the range, say, 0.005 to 0.05%; in terms of time expended this is about the choice we face in this case.

Again, in over 60 specimens from in and near a transition between "granodiorite" and "gabbrodiorite" in Norfolk County, Massachusetts, the replacement habit of quartz is always prominent. These rocks are extensively altered and I believe that from an examination of the thin sections most geologists—myself included—would be willing to regard the metasomatic or hydrothermal introduction of quartz as a factor of first importance in determining their composition. Yet nearly all of my specimens contain less than 6 or more than 28 per cent of quartz; the introduction of quartz, apparently so extensive, has not even masked, much less eliminated, one of the most prominent original differences between the dominant members of the complex. All of the rocks are now a little richer in quartz than they may once have been, but some, and possibly a good deal, of this excess quartz may have formed by decomposition of minerals already present. Hydrothermally introduced quartz can hardly amount to more than a few per cent of the total rock.

These results will be described in detail in a later report; they are mentioned here only as an illustration of the utility of moderately precise quantitative estimates. The range of quartz content is here very wide, so that a precision error of 1% in each analysis is not of much consequence. Forty or fifty moderately precise analyses of well chosen samples provide grounds for an extremely useful, if rather rough, estimate of the general importance of hydrothermal quartz; 10 or 20 analyses would give no more than an indication, regardless of their precision. For the same investment in time there is a much greater return from numerous moderately precise analyses—providing their precision is known—than there would be from a few excellent analyses.

The point counter described in this note may be used either for very detailed work or for the rapid, moderately precise estimates which seem to me of so much greater present importance. In terms of both time and money it brings quantitative modal analysis within reach of every petrographic laboratory.

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THE UNIT CELL AND SPACE GROUP OF CHILDRENITE

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Abstract

The unit cell constants and the space group of childrenite, $AlPO_4 \cdot Fe(OH)_2 \cdot 2H_2O$, have been determined by the Buerger precession method with the following results: $a = 10.38$Å, $b = 13.36$ Å, $c = 6.911$ Å; $a:b:c = 0.7766:1:0.5173$; $Z = 8$; calculated density = 3.186 g./cc.; space group *Bba*2.

Introduction

Crystals of childrenite, $AlPO_4 \cdot Fe(OH)_2 \cdot 2H_2O$, are orthorhombic with axial ratio, determined from morphological data (1), $a:b:c = 0.7780:1:0.52575$ and a specific gravity of 3.18–3.24. The specimens examined in the present study of the unit cell constants and space group were from the type locality of Tavistock, Devonshire, England. They were kindly supplied by Dr. Clifford Frondel from the Mineralogical Collection at Harvard University (specimen 80618).

Assuming the morphological axes to coincide with the corresponding structural ones, photographs were taken of the zero, first and second reciprocal lattice levels normal to each of the *a*, *b* and *c* axes using Professor M. J. Buerger's precession camera (2). Cone axis photographs (2) served as a guide to the reciprocal lattice spacings and hence as a check on the numerical labelling of the levels examined. Both copper (nickel foil filter) and molybdenum (zirconium oxide filter) were employed in the course of the investigation. Reciprocal lattice spacings and angles were measured with the instrument devised by Professor Buerger (3) for precession films. The approximate accuracy of the precession instrument and of the film measuring device was tested with cone axis and zero level photographs obtained with the *a* and *b* (orthohexagonal) axes of a (rather large) crystal of α-quartz as precession axes. A more rigid test of the precision attainable with the precession instrument will be described in another communication.

Results

Space Group

Typical precession photographs of childrenite are reproduced in Figs. 1 to 6 inclusive. The geometry of all the levels examined is summarized in Fig. 7 in which the central areas of the plane nets for the zero, first and second reciprocal lattice levels normal to each of the *a*, *b*, and *c* axes are represented. In this diagram, extinctions not due specifically to space group symmetry elements as well as the relative intensities of the actual

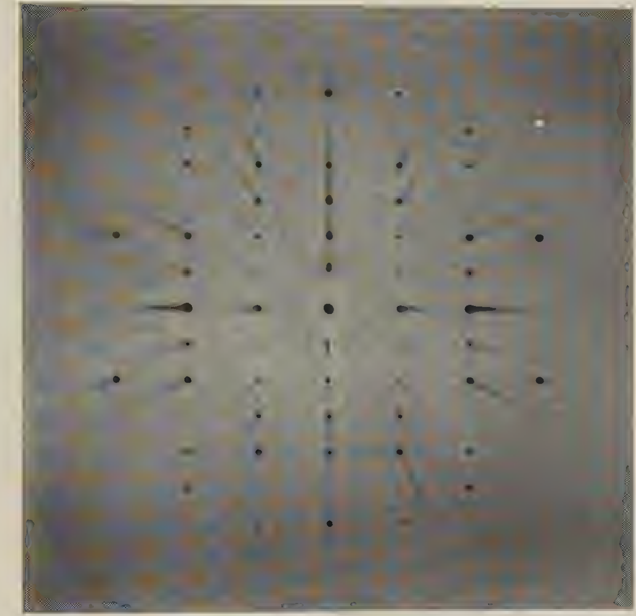

Fig. 1. Childrenite. *a* axis, zero level (Mo) (c^* horizontal).

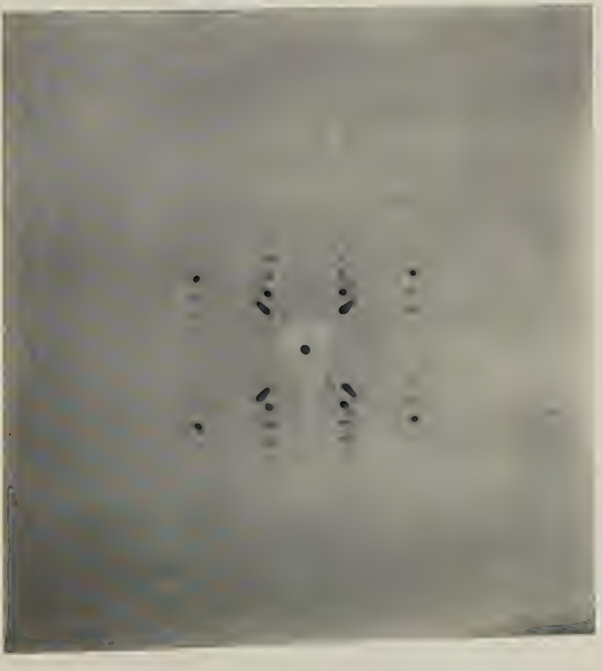

Fig. 2. Childrenite. *a* axis, first level (Mo) (c^* horizontal).

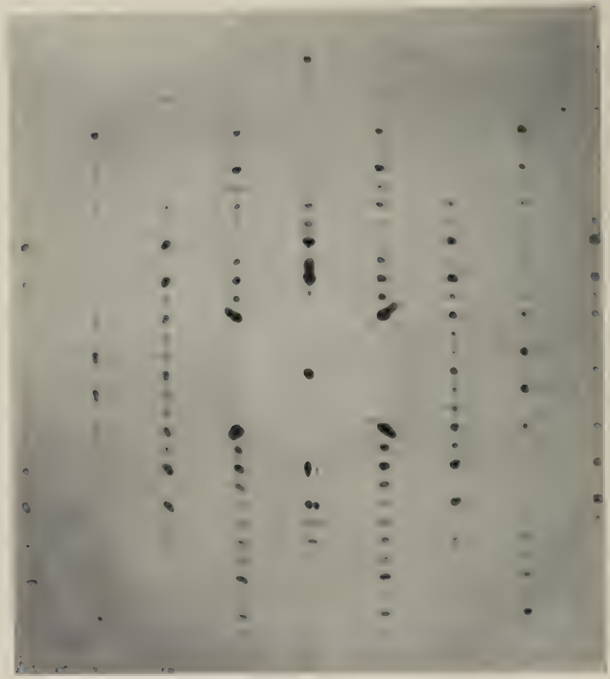

FIG. 3. Childrenite. *a* axis, second level (Mo) (*c** horizontal).

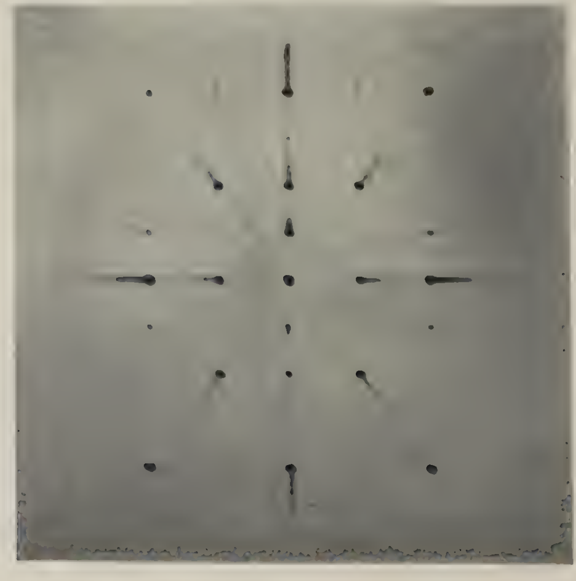

FIG. 4. Childrenite. *b* axis, zero level (Mo) (*c** horizontal).

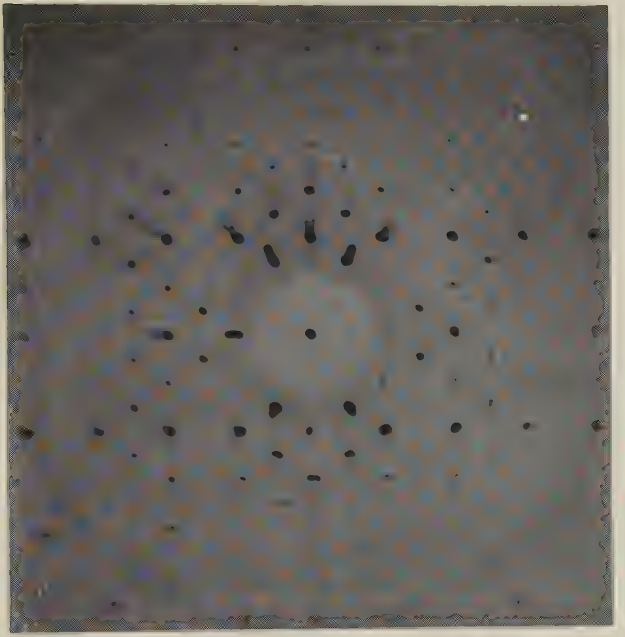

Fig. 5. Childrenite. *b* axis, second level (Mo) (c^* horizontal).

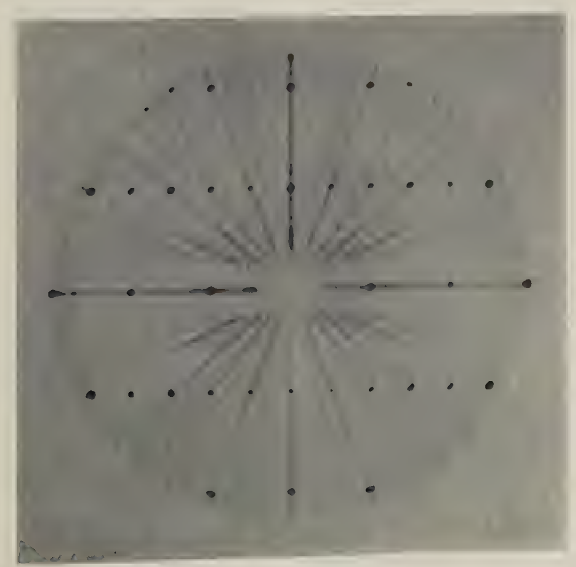

Fig. 6. Childrenite. *c* axis, zero level (Cu) (b^* horizontal).

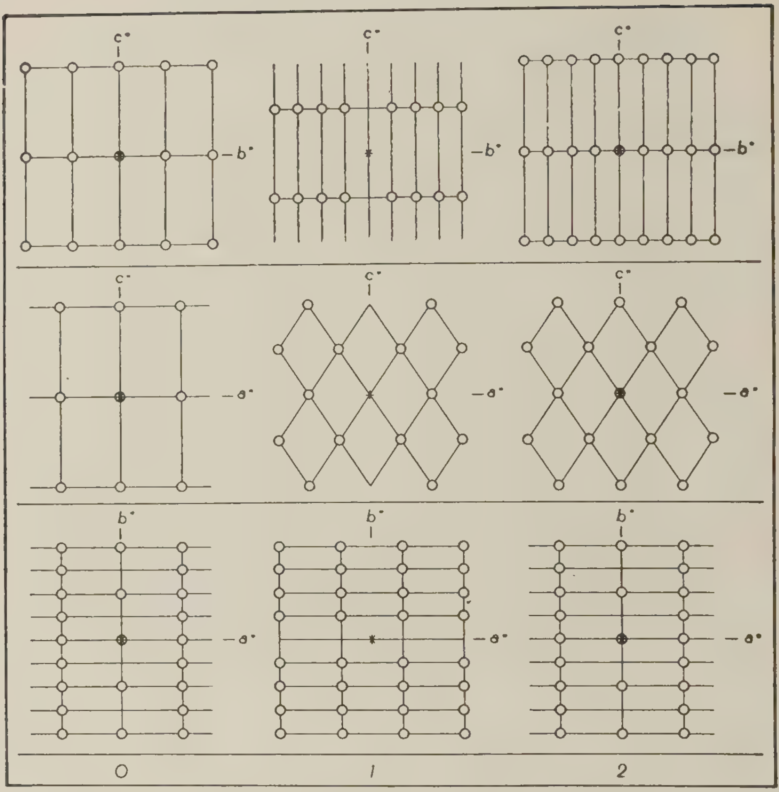

FIG. 7. 0,1,2 level reciprocal lattice nets shown by (top row)a, (middle row)b, (bottom row)c axis precession photographs of childrenite.

diffraction spots on the films have been ignored. The center of each net is marked with a star.

By simple inspection of the b^*c^* and a^*b^* nets it is apparent that the direct cell is b-side centered. The doubled spacing of the rows parallel to c^* in the zero level b^*c^* net indicates a glide plane of component $b/2$ perpendicular to the a axis. This glide plane also accounts for the 2_1 screw axis along b which produces the doubled translation along b^* in the zero level a^*b^* net. In the a^*c^* nets the change from the diamond net characteristic of the upper levels to the rectangular net shown by the zero level reveals a glide plane of component $a/2$ (or the equivalent $c/2$, since the cell is b-side centered) perpendicular to the b axis. In each two-dimensional net the directions of the two reciprocal axes are mutually perpendicular and are symmetry lines.

Thus the diffraction symmetry is *mmm* and the diffraction symbol is *mmmBba*–so that the space group must be either *Bba*2 (C_{2v}^{17}) or *Bbam* (D_{2h}^{18}). The axes of the structural unit cell, therefore, are in harmony with those assigned from morphological data. Childrenite crystals were tested for piezoelectricity by Dr. Frondel and a small but positive effect was obtained. The centrosymmetrical space group, *Bbam*, thus is eliminated and childrenite must be assigned to the space group, *Bba*2.

Unit Cell Constants

The best *a*, *b* and *c* axis zero level precession photographs obtained with copper radiation were selected for measurement. In each case the angles between rows of the net parallel to the reciprocal axes were determined and confirmed the orthogonality of the lattice. The distances between successive pairs of rows parallel to a given axis were measured to 0.05 mm. and averaged. This value was divided by the magnification factor ($F=6.00$ cm.) to give the spacing in reciprocal lattice units, or double the spacing where the reciprocal lattice translations were doubled due to space group extinctions.

The reciprocal lattice spacings are summarized in Table 1.

TABLE 1

Precession Axis	d_a^*	d_b^*	d_c^*
a	—	0.115_5	0.223_0
b	0.148_3	—	0.223_2
c	0.148_9	0.115_2	—
Average	0.148_6	0.115_4	0.223_1

Using the value 1.5418 Å (4) for λ (CuKα), the direct cell translations are:

$$a = 1.5418/0.1486 = 10.38 \text{ Å}‡$$
$$b = 1.5418/0.1154 = 13.36 \text{ Å}‡$$
$$c = 1.5418/0.2231 = 6.911 \text{ Å}‡$$

and the axial ratio:

$$a:b:c = 0.7766:1:0.5173.$$

The volume (V) of the unit cell $=a\times b\times c=958.0$ Å^3.

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‡ The numerical values differ slightly from those reported at the 1947 Spring Meeting of The Crystallographic Society of America (5) because the direct lattice translations have been recomputed from the measured reciprocal lattice spacings in terms of the presently accepted Ångstrom unit instead of the kX unit.

Taking the specific gravity as 3.2, the formula weight (M) as 229.8 (Al, 26.97; P, 30.98; Fe, 55.85; 7O, 112.00; 4H, 4.032) chemical atomic mass units and the density $(\rho)=1.6602ZM/V$(4), the number of formula units per cell

$$Z = \frac{3.2 \times 958.0}{1.660 \times 229.8} = 8.035 \approx 8.$$

With $Z=8$, the density calculated from the foregoing formula is 3.186 g./cc.

Work is continuing on eosphorite into which childrenite graduates by replacement of Fe by Mn. Delay has been occasioned by a change in laboratories and by the fact that the smallest crystals of eosphorite so far examined have turned out to be multiple growths with so many individual members that even precession photographs could not be measured accurately.

Acknowledgments

I am indebted to the John Simon Guggenheim Memorial Foundation for a Fellowship and to McGill University, Montreal, for leave-of-absence. I wish to express my appreciation to Professor M. J. Buerger for the opportunity of working in his laboratory at the Massachusetts Institute of Technology and for the help and many kindnesses extended to me by Professor Buerger and by other members of the staff and graduate students during my visit.

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THE UNIT CELL AND SPACE GROUP OF PROBERTITE

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Abstract

The unit cell constants and the space group of probertite, $Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 10H_2O$, have been determined by the Buerger precession method with the following results: $a=13.88$ Å, $b=12.56$ Å, $c=6.609$ Å, $\beta=107°40'$; $a:b:c=1.1053:1:0.5263$; $Z=2$; calculated density$=2.126$ g./cc.; space group $P2_1/n$.

Introduction

Probertite, $Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 10H_2O$, is monoclinic, has a radiating prismatic habit, perfect (110) cleavage and specific gravity of 2.141 (1). Axial ratios have not been determined, due presumably to the habit which makes the discovery of well-formed single crystals problematical. I am indebted to Professor Clifford Frondel for a specimen (No. 94710) from the Mineralogical Collection of Harvard University. The source locality was Lang, California.

X-Ray Data and Results

Assuming the cleavage plane to have been identified correctly from the point of view of the structural cell as (110), zero, first and second reciprocal lattice level photographs normal to the *a* and *b* axes were obtained with Professor M. J. Buerger's precession camera (2). Copper radiation, with a nickel foil filter, was employed. The films were measured with the appropriate measuring device (3).

The zero and first level photographs are reproduced in Figs. 1, 2, 3, 4 and it will be seen at once that the small specimen examined was a multiple growth consisting of several individuals rather than a single crystal. Some leakage of beta radiation through the foil also is apparent. The films illustrate an important application of the precession method based on the fact that there is no distortion of the plane nets in the photographs of the reciprocal lattice levels. Diffraction spots on a zero level photograph arising from a single crystal can be recognized without difficulty even in the presence of spots due to other individuals that may be present. The latter can be ignored thereafter and precise orientation of the selected crystal can be completed with the aid of subsequent precession photographs (2, p. 21 *et seq.*).

Since only a limited number of unit cell and space group studies have been made with the precession instrument the experimental data obtained in the present instance are reproduced in full. They illustrate typical

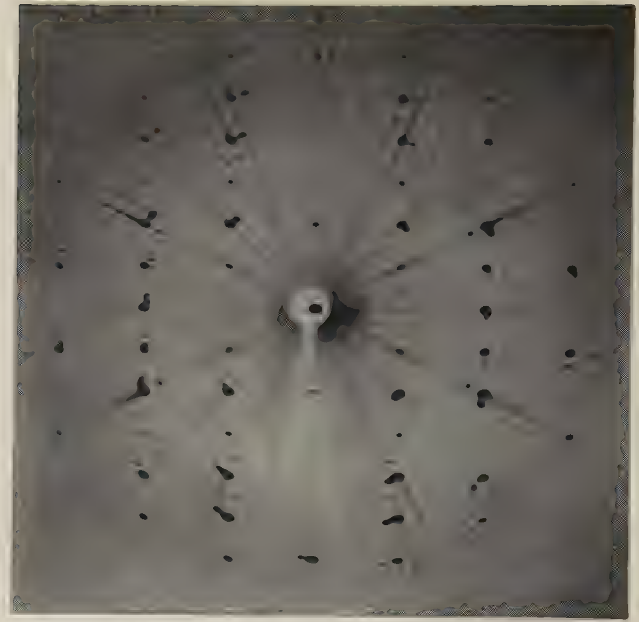

FIG. 1. Probertite. *a* axis, zero level (Cu) (c* horizontal).

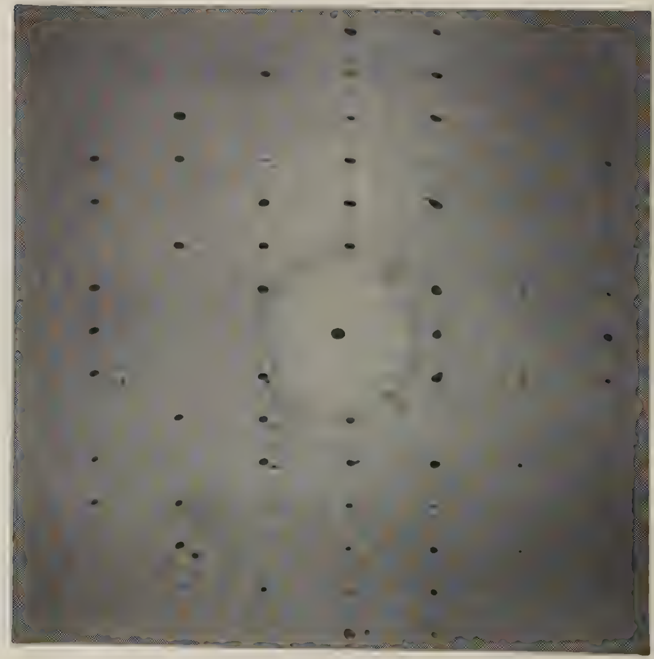

FIG. 2. Probertite. *a* axis, first level (Cu) (c* horizontal).

FIG. 3. Probertite. *b* axis, zero level (Cu) (c* horizontal).

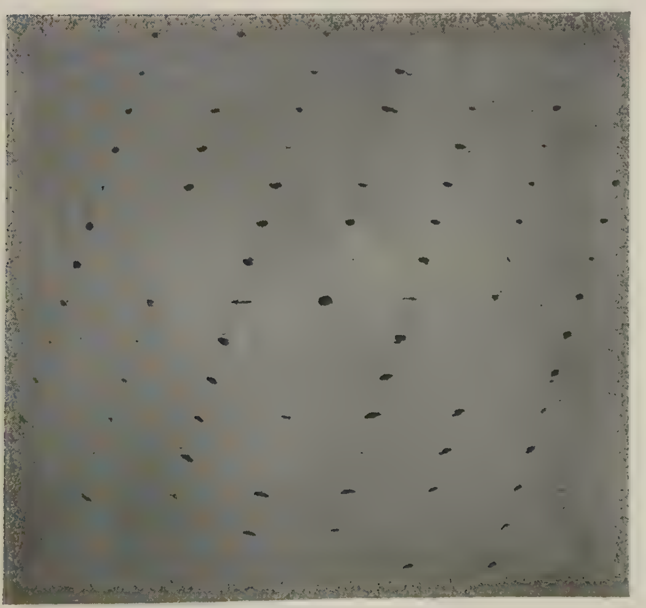

FIG. 4. Probertite. *b* axis, first level, (Cu) (c* horizontal).

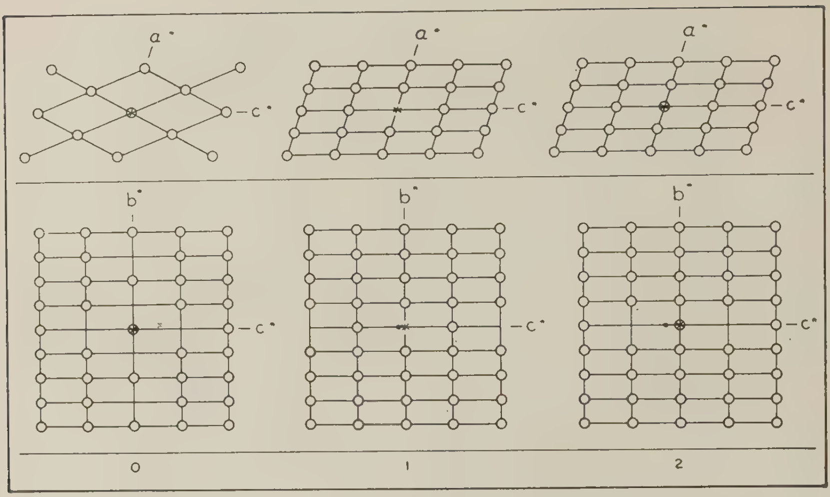

FIG. 5. 0,1,2 levels reciprocal lattice nets shown by (upper row)*b* and (lower row)*a* axis precession photographs of probertite. (Diffraction symbol $(2/m)P(2_1/n)$.)

measurements on average precession films and show that the use of a measuring device that reads (with verniers) to five minutes of arc and 0.05 mm. length is more than justified.

a AXIS, ZERO LEVEL

Angles between b^* and c^*

Scale reading	Angle
89°15′	—
359°00′	90°15′
268°50′	90°10′
178°55′	89°55′
89°15′	89°40′
average	90°00′

The net is orthogonal. Deviations from 90°00′ can be ascribed to experimental error particularly since + and − deviations, respectively, are observed for adjacent (and not opposite) angles.

c^* translation (t_c^*) and spacing (d_c^*)

(Perpendicular distances between successive rows of spots; the second set of each Ft^* measurement was obtained after rotating the film through 180°)

Scale reading (cm.)	Ft_c^* (cm.)	Scale reading (cm.)	Ft_c^* (cm.)
12.030	—	11.980	—
10.560	1.470	10.510	1.470
9.080	1.480	9.040	1.470
7.620	1.460	7.580	1.460
6.145	1.475	6.105	1.475
average	1.471	*average*	1.469

average both sets = 1.470 cm.

$$Fd_c^* = Ft_c^* \sin \beta^*$$
$$= 1.470 \sin 72°20' = 1.4007 \text{ cm.}$$

b^* translation (t_b^*) and spacing (d_b^*)

Scale reading (cm.)	$Ft_b^*=Fd_b^*$ (cm.)	Scale reading (cm.)	$Ft_b^*=Fd_b^*$ (cm.)
12.600	—	12.885	—
11.860	0.740	12.160	0.725
11.125	0.735	11.430	0.730
10.385	0.740	10.690	0.740
9.650	0.735	9.970	0.720
8.900	0.750	9.220	0.750
8.175	0.725	8.480	0.740
7.435	0.740	7.750	0.730
6.695	0.740	7.010	0.740
5.965	0.730	6.265	0.745
5.230	0.735	5.525	0.740
average	0.737	*average*	0.736

average both sets, $Fd_b^*=0.7365$ cm.
$d_b^*=0.7365/6.00=0.1228$ reciprocal lattice units.

b AXIS, ZERO LEVEL

Angles between a^* and c^*

Scale reading	β^*	β
17°40′	—	—
269°55′	—	107°45′
197°40′	72°15′	—
90°05′	—	107°35′
17°40′	72°25′	—
average	72°20′	107°40′

c^* translation (t_c^*) and spacing (d_c^*)

Scale reading (cm.)	$Ft_c^*=Fd_c^*$ (cm.)	Scale reading (cm.)	$Ft_c^*=Fd_c^*$ (cm.)
11.835	—	11.895	—
10.430	1.405	10.490	1.405
9.030	1.400	9.095	1.395
7.640	1.390	7.695	1.400
6.250	1.390	6.290	1.405
average	1.396	*average*	1.401

average both sets, $Fd_c^*=1.3985$ cm.
from a axis, zero level, $Fd_c^*=1.4007$ cm.
average, $Fd_c^*=1.3996$ cm.
$d_c^*=1.3996/6.00=0.2333$ reciprocal lattice units.

a^* translation (t_a^*) and spacing (d_a^*)

Scale reading (cm.)	$Ft_a^* = Fd_a^*$ (cm.)	Scale reading (cm.)	$Ft_a^* = Fd_a^*$ (cm.)
13.115	—	12.340	—
12.440	0.675	11.670	0.670
11.780	0.660	11.015	0.655
11.115	0.665	10.350	0.665
10.440	0.675	9.680	0.670
9.780	0.660	9.015	0.665
9.105	0.675	8.350	0.665
8.445	0.660	7.685	0.665
7.770	0.675	7.015	0.670
7.115	0.655	6.345	0.670
6.450	0.665	5.685	0.660
5.780	0.670	5.010	0.675
average	0.666_9	*average*	0.666_4

average both sets, $Fd_a^* = 0.6667$ cm.

$d_a^* = 0.6667/6.00 = 0.1111$ reciprocal lattice units.

Taking λ (CuKα) as 1.5418 Å (4), the formula weight (M) as 702.5 (2Na, 45.994; 2Ca, 80.16; 10B, 108.2; 20H, 20.160; 28O, 448.000) chemical atomic mass units and the density $(\rho) = MZ/1.6602V$ g./cc. (4) the direct cell constants are as follows:

$$a = \lambda/d_a^* = 1.5418/0.1111 = 13.88 \text{ Å}‡$$

$$b = \lambda/d_b^* = 1.5418/0.1228 = 12.56 \text{ Å}‡$$

$$c = \lambda/d_c^* = 1.5418/0.2333 = 6.609 \text{ Å}‡$$

$$\beta = 107°40'$$

$$a:b:c = 1.1053:1:0.5263$$

$$V \text{ (volume of unit cell)} = abc \sin\beta = 1097.2 \text{ Å}^3$$

$$Z \text{ (formula units per cell)} = \rho V/1.6602M = \frac{2.141 \times 1097.2}{1.6602 \times 702.5} = 2.014 \approx 2.$$

calculated density = 2.126 g./cc.

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‡ These values differ slightly from those reported at the 1947 Annapolis meeting of The Crystallographic Society of America (5) because they have been recomputed in terms of the currently adopted Å unit instead of the kX unit.

The central areas of the a^*c^* and b^*c^* plane nets for the zero, first and second reciprocal lattice levels normal to the b and a axes, respectively, are shown diagrammatically in Fig. 5, where extinctions other than those due to space group symmetry elements have been ignored as well as the relative intensities of diffraction spots. The center of each net is indicated by a star, which represents a point of intersection of the reciprocal lattice axis that is not contained within the net itself. The dot to the left of the center in the first and second level b^*c^* nets shows the point of intersection of the a (precession) axis, the increasing magnitude of the off-set with increasing height of the level being due to the angle ($90°-\beta^*$) between a and a^*; in the other nets illustrated in Fig. 5 the point of intersection of the precession axis coincides with the center of the net.

It is at once apparent that the a^*c^* nets are characterized by a center of symmetry and the b^*c^* nets by two symmetry lines at right angles; the diffraction symmetry, therefore, is $2/m$. A comparison of the nets for the different levels shows that the direct cell as selected is a primitive one. The change from the diamond-like net for the b axis zero level to the rectangle-like net of the upper levels reveals an n glide plane of component $a/2+c/2$ perpendicular to the b axis. The doubled translation along b^* in the a axis zero level net indicates a 2_1 screw axis along b. The diffraction symbol, therefore, is $(2/m)P(2_1/n)$ and the space group is $P2_1/n$ (C_{2h}^5).

ACKNOWLEDGMENTS

This work was carried out in Professor M. J. Buerger's laboratory of x-ray crystallography at the Massachusetts Institute of Technology. I wish to express my thanks to Professor Buerger and to other members of the staff for many courtesies during my visit. I am indebted to the John Simon Guggenheim Memorial Foundation for a Fellowship and to McGill University, Montreal, for leave-of-absence.

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LIQUID INCLUSIONS IN HALITE AS A GUIDE TO GEOLOGIC THERMOMETRY

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Abstract

The gaseous phase of liquid inclusions in sedimentary halite disappears between 70 and 100° C. The interpretation of liquid inclusions in geologic thermometry is discussed.

Introduction

Primary liquid inclusions have been used widely as an indication of the temperature of formation of minerals. The fundamental assumption postulated by Sorby in 1858 has been summarized by Ingerson (1947, p. 376) as follows: "The fundamental assumption has not changed since Sorby's time—that a liquid inclusion cavity was just filled with fluid at the temperature and pressure under which it was formed. These conditions and the composition of the solution, determine the degree of filling of the cavity as it is observed at room temperature. If a crystal containing such inclusions is heated, the liquid will expand and fill the cavity at the temperature of formation if the original pressure did not exceed significantly the vapor pressure of the solution." Ingerson further states (p. 377): "It is necessary to distinguish primary and secondary liquid inclusions in a mineral. Only the primary ones record the temperature at which the mineral crystallized; secondary inclusions may give an indication of prevailing temperature during a later reworking."

Occurrence of Inclusions in Halite

The writers have studied the effects of heat on liquid inclusions in halite. The halite specimens were collected by Mr. R. A. Hartenberger of the University of Kansas from the 900 foot level of the American Salt Co. mine at Lyons, Kansas. The halite was taken from dry, massive, well-stratified, undeformed salt beds within the Wellington formation of Permian age. About 150 feet of unmined salt overlies the horizon from which the samples were taken. Liquid inclusions are widespread throughout the salt beds, but, in some places, are much more numerous than in others. Many of the specimens studied have a large number of liquid inclusions—in some cases over ten per cubic inch. Some of the inclusions are quite large, several of those studied having a surface area of over seven square millimeters. Volumes of the inclusion cavity and of the gaseous phase (bubble) within the cavity have been calculated on the basis of

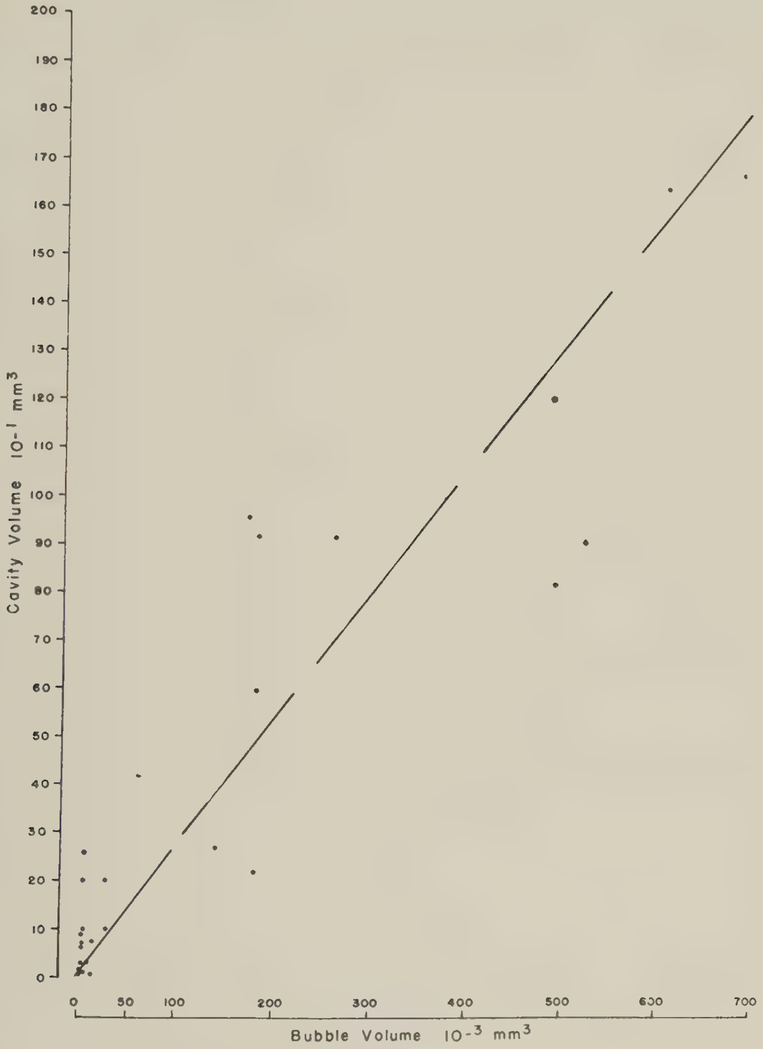

FIG. 1. Relation of bubble volume to volume of inclusion cavity.

mean diameters measured on a cleavage surface. Though this method gives an accurate measure of the bubble volume, the cavity volumes calculated by this method represent only a first approximation to the true volume since the inclusion cavities are very irregular. Nevertheless, in spite of the fact that the volume of the inclusion cavity cannot be calculated as accurately as the volume of the gaseous phase, Figs. 1 and 2 show that there is a reasonably good correlation between the calculated volume

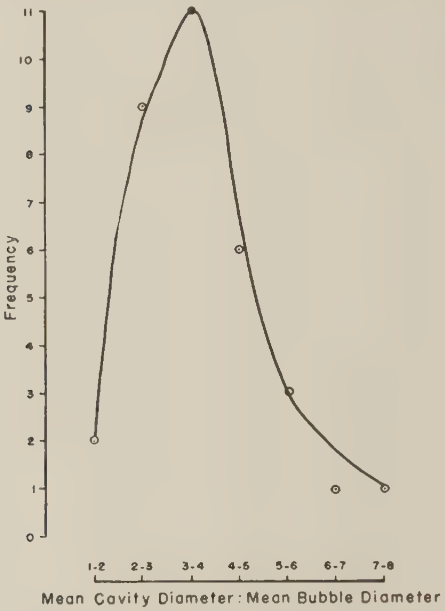

FIG. 2. Relation of mean inclusion cavity diameter to mean bubble diameter.

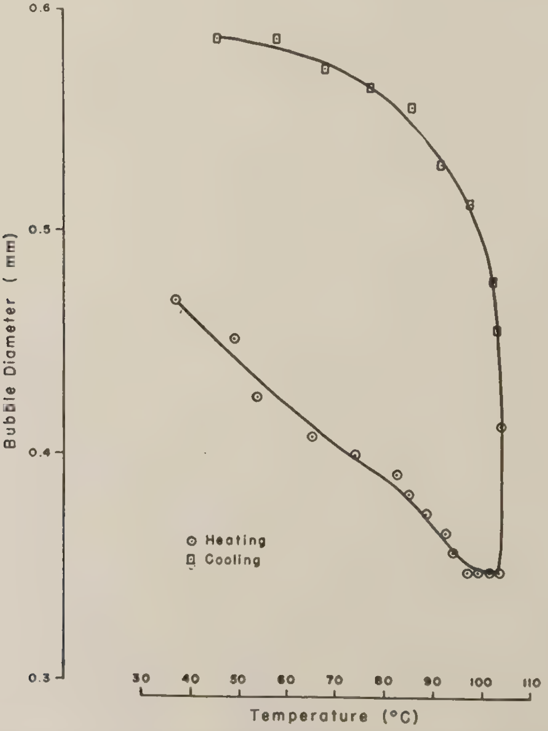

FIG. 3. Heating-cooling curves for halite inclusion from which liquid escaped during heating.

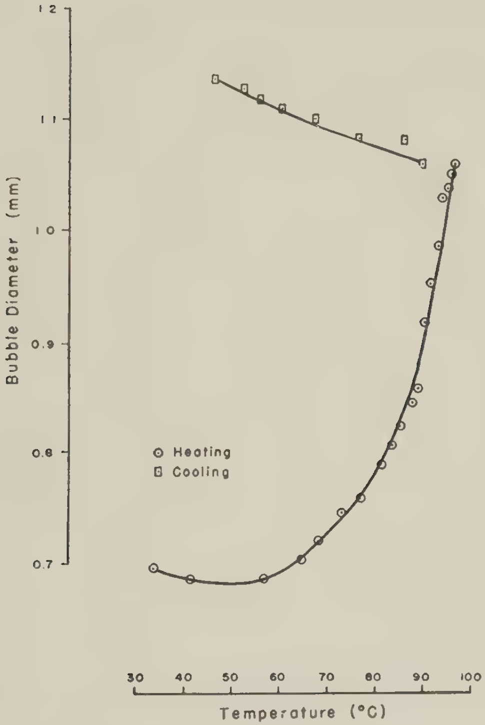

FIG. 4. Heating-cooling curves for halite inclusion from which liquid escaped during heating.

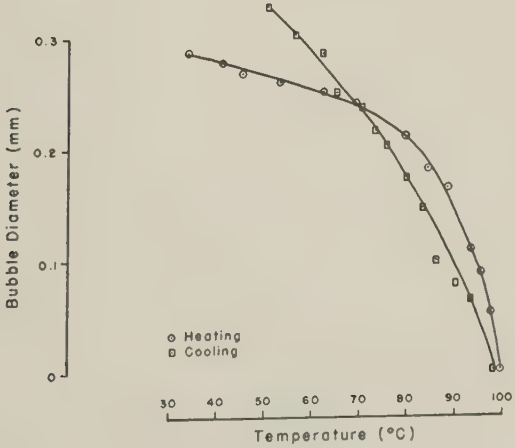

FIG. 5. Heating-cooling curves for halite inclusion.

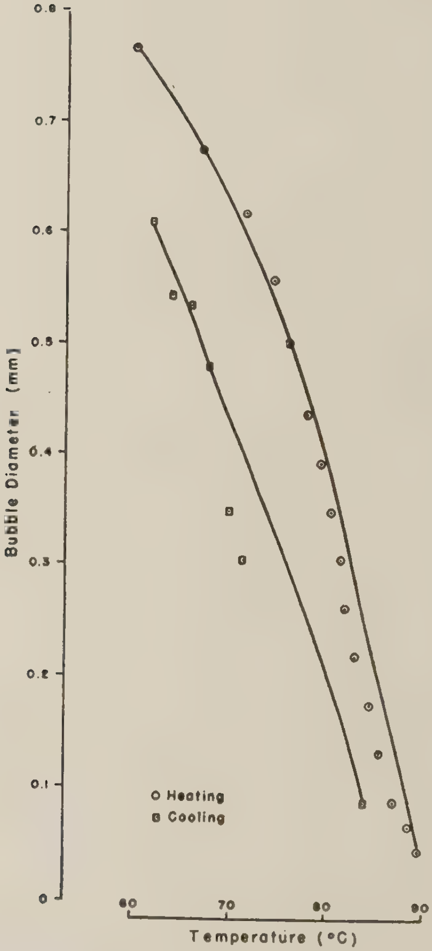

FIG. 6. Heating-cooling curves for halite inclusion.

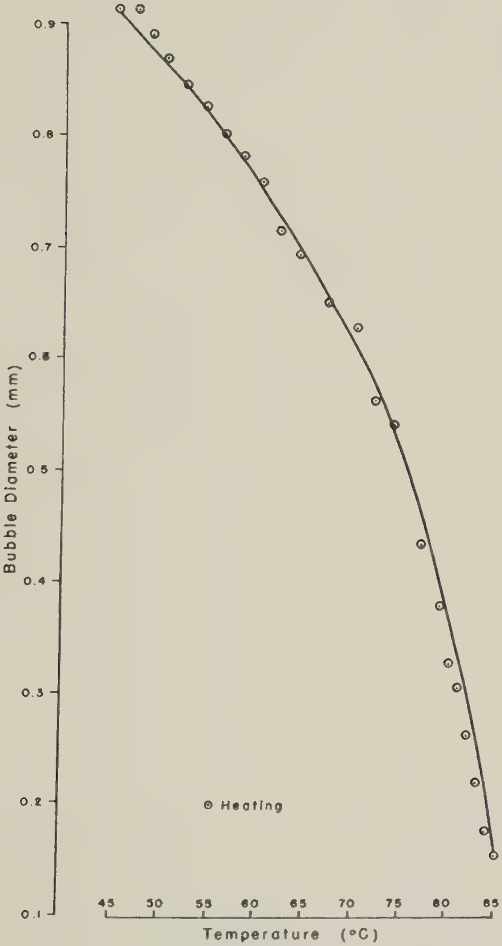

FIG. 7. Heating curve for halite inclusion.

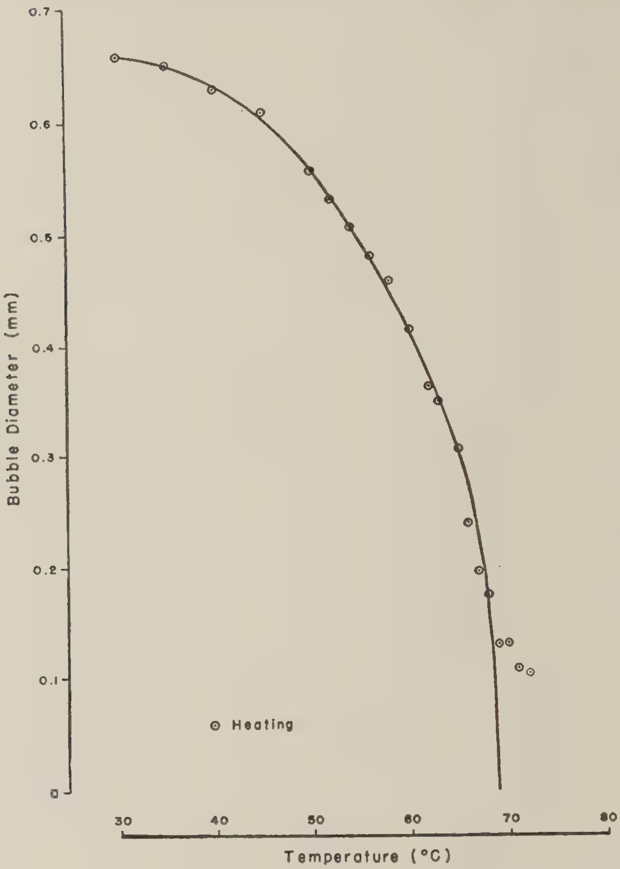

FIG. 8. Heating curve for halite inclusion.

of the inclusion and of the gaseous phase. The following factors then indicate that the halite inclusions were primary: (1) The specimens come from dry, well-stratified, undistorted strata beneath 150 feet of unmined overlying salt. (2) There is a reasonably good correlation between the volume of the inclusion and the volume of the gaseous phase.

GEOTHERMAL DATA

Cleavage fragments of halite containing fluid inclusions were heated on a heating stage (Ingerson, 1947, p. 377) and the decreasing size of the bubble plotted against temperature until the vapor phase vanished. The halite was then allowed to cool and the cooling curve was plotted. Since there was very little thermal lag, the heating and cooling curves were, in most cases, nearly identical. In a few cases, the pressure created by heating the inclusions forced the liquid out along incipient cleavage plane breaks which developed unavoidably during the preparation of the original cleavage fragments. In such cases, the heating curves had the form shown in Figs. 3 and 4. In all other cases, however, the heating and cooling curves have a regular form as shown by Figs. 5 to 9. It will be noted from Figs. 5 to 9 that the vapor phase vanishes between 70 and 100° C.

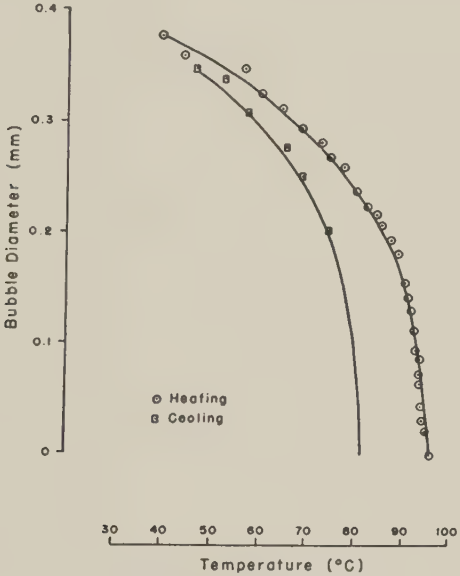

FIG. 9. Heating-cooling curves for halite inclusion.

CONCLUSIONS

According to previous interpretations, the temperature at which the gaseous phase vanishes would be regarded as the minimum temperature of formation of halite and as the temperature of the solvent from which precipitation occurred. It is obvious, however, that the bodies of water from which the sedimentary halite was deposited could not have had a general temperature of 70–100° C. Ingerson (personal communication) notes that a temperature of "70° has been recorded in one of the lakes near the Caspian Sea where salt is crystallizing rapidly" and that temperatures have been reported "in artificial salt lakes in the New Mexico potash fields so high that they burn one's hands." Presumably such temperatures are found adjacent to the salt-solvent contact. The most obvious explanation which comes to mind is that these high temperatures have resulted from the heat of crystallization of the salt. In the Kansas salt deposits, however, the only mineral which crystallized from the sea water was halite, which has a very low heat of crystallization. There is also some evidence that the Kansas salt deposits may not have resulted from such rapid crystallization and hence may not represent conditions analogous to those mentioned by Ingerson. It is difficult to understand, moreover, how this relatively small amount of heat could remain confined to the zone adjacent to the crystallizing salt to the extent of raising the temperature many degrees above that normally found in sea water. Furthermore, experiments on the heat of crystallization from saturated sodium chloride and potassium chloride brines (using sensitive thermocouples) indicates no perceptible increase in temperature. The high temperatures noted by Ingerson may represent, therefore, exothermic reactions rather than heat of crystallization. Nevertheless, if in a lake or ocean, thermal effects can raise the temperature of formation of crystals so markedly above the temperature of the major portion of the solvent, it would seem probable that, in any system of relatively poor thermal circulation (such as a vein), these thermal effects might be an even more effective factor in raising the temperature of formation of crystals above the temperature of the major portion of the solvent. It is suggested that, if the liquid inclusion method is a valid guide to geologic thermometry, the method gives, after pertinent pressure corrections, only the temperature of the solution at the surface of the crystallizing material and that the general temperature of the mineralizing solutions may be much below that indicated by the liquid inclusions.

Acknowledgments

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THE DISTRIBUTION OF ACCESSORY ELEMENTS IN PEGMATITES. I. THEORY

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ABSTRACT

A mathematical theory for the distribution of accessory elements in pegmatites is derived. The admittance of accessory elements by crystal lattices, the distribution of accessory elements as a function of the distance from the wallrock-pegmatite contact, and the effect of disturbing factors on the cooling history of a pegmatite are discussed. The theory is illustrated with an artificial example and suggestions are made relative to its testing by experimental data. It is proposed that such testing will elucidate the mechanism of pegmatite formation.

INTRODUCTION

Theoretically the distribution of elements accessory to the mineral types of pegmatites is dependent on the mode of formation of the pegmatite. The problem of the origin of pegmatites can therefore be approached through a study of the distribution of these elements. In this paper a theory has been formulated for this distribution. Since quantitative field and laboratory tests of the theory developed are possible, this theory should serve to clarify and improve the existing concepts of the origin of pegmatites.

Theories for the origin of pegmatites have been numerous and divergent. In the first quarter of the nineteenth century Charpentier (1823) proposed magmatic injection and crystallization. Later Credner (1875) suggested "lateral secretion." In the 1920–1930 period students of complex pegmatites such as F. L. Hess (1925), Schaller (1925), and Landes (1925) favored replacement of an earlier simple "magmatic" pegmatite by hydrothermal solutions. The detailed mapping of a great number of pegmatites by the Federal Survey in the period 1939–1945 has resulted in the best documented picture of lithologic units in pegmatites. In their paper, Cameron, Jahns, McNair, and Page (to be published) note the existence of units called replacement bodies and fracture fillings, but find that in most areas these are quantitatively insignificant compared to zones ("successive shells, complete or incomplete, that reflect to varying degrees the shape or structure of the pegmatite body. Where ideally developed they are concentric about an innermost core"). These authors "adopt the theory that the zones have developed from the walls inwards, essentially by fractional crystallization and incomplete reaction in a restricted system."

If such an origin is assumed for the pegmatites, the distribution of accessory elements can be more easily explained than if one assumes the replacement mechanism. In the physical chemical derivation to follow, it is assumed that zoned pegmatites are formed by magmatic injection and fractional crystallization, but the effect of other mechanisms is also considered. If suitable experimental data fit the distribution of accessory elements as predicted for the Cameron, Jahns, McNair, Page concept of origin, it will be a strong support for their theory.

Previous experimental work on the distribution of trace elements in pegmatites has been very limited. Ahrens (1947; to be published), Hahn and Walling (1938), Mattauch (1937), have determined the content of strontium and rubidium in specimens of lepidolite, muscovite, phlogopite, pollucite, and feldspar. Bray (1942) has completed a regional study of trace element distribution. However, quantitative studies of the variation of the content of accessory elements in the same pegmatite, not only from one mineral to another but also in any given mineral at different points in the pegmatite, are few in number.

The theoretical treatment of the distribution of accessory elements in minerals of pegmatites will be divided into three parts.

(1) The distribution of accessory elements as a function of the ease of entrance, or admittance, of the element into growing crystal lattices.

(2) The distribution of accessory elements in a particular lattice type as a function of the distance from the wallrock pegmatite contact.

(3) The effect of loss or addition of material, convection, shattering, veining, and replacement in the cooling history of pegmatites.

Admittance of Accessory Elements by Crystal Lattices and Crystal Aggregates

On the surface of any ionic crystal there are sites at which cations and anions can be added. In a suitable medium ions will be constantly arriving at and leaving from these points. When the number of ions arriving is greater than the number leaving, the crystal is growing. Incorporation of foreign ions into a crystal possessing an ionic lattice will occur when foreign ions arrive and stay at sites on the crystal surface. There are two possible interpretations for the incorporation of foreign ions: (1) the foreign ion can be considered as replacing an ion of the main lattice constituent already lodged on the surface of the crystal, and (2) the foreign ion can be thought of as capturing an empty site which would normally be occupied by an ion of the main lattice constituent.

The mechanism of foreign-ion incorporation has been variously interpreted by authors on the basis of either of these mechanisms in treating such widely differing phenomena as foreign-ion incorporation in aqueous solutions and in crystallizing melts.

However, these two processes are essentially the same since incorporation of foreign ions is a dynamic process and depends only on the relative ease with which the two ions can attach themselves to the available sites, and on the geometric difficulties of closing the next layer above the foreign ion in the growth of the crystal. It is not surprising, therefore, that the equations relating the concentration of the foreign ion in the lattice as a function of the amount of material crystallized are the same whichever interpretation is used as the point of departure.

Two excellent examples of the applicability of this type of reasoning are to be found in the incorporation of radium ions in a $BaSO_4$ precipitate and in the incorporation of potassium and copper ions in crystals of NaCl grown from a melt.

Similar lines of reasoning lead to analogous conclusions for the case of non-ionic lattices. In that case the unit cell containing the foreign element acts in the same fashion as the foreign ion, and surface energy as well as geometric considerations will be related to this unit cell rather than to the foreign ion alone.

Incorporation During Precipitation from Dilute Aqueous Solutions

The mechanism for foreign element incorporation is clearly illustrated by the system $BaSO_4$—$RaSO_4$, investigated by Hoskins and Doerner (1928). In the experiments of these authors H_2SO_4 was added so that the solubility product, K, of $BaSO_4$, but not that of $RaSO_4$, was exceeded. It was found that the $RaCl_2$ remaining in solution after precipitation of the $BaSO_4$ was less than the original amount. Some radium ions must therefore have been included in the $BaSO_4$ precipitate. According to Hoskins and Doerner (1928) the following reaction had taken place.

$$BaSO_4 + RaCl_2 \rightleftarrows RaSO_4 + BaCl_2.$$

This means that at equilibrium there is exchange of radium ions in solution with barium ions in the precipitate and vice versa; i.e., one particle is removed from the crystal surface for each one added. The relation between the concentration of the four components of the system at equilibrium can be expressed by the equation

$$\frac{A_{(\mathrm{Ra}^{++})\ \text{on surface}}}{A_{(\mathrm{Ba}^{++})\ \text{on surface}}} = K\frac{A_{(\mathrm{Ra}^{++})\ \text{in solution}}}{A_{(\mathrm{Ba}^{++})\ \text{in solution}}}$$

where A stands for the activity of the components (see Taylor, 1942, p. 374 ff.). In the following derivations it will be assumed that the activities can be replaced by the concentration of the specific components. The above expression therefore becomes

$$\frac{\text{No. of Ra}^{++}\text{ on surface}}{\text{No. of Ba}^{++}\text{ on surface}} = K\frac{[\mathrm{Ra}^{++}]\text{ in solution}}{[\mathrm{Ba}^{++}]\text{ in solution}}. \qquad (1)$$

The magnitude of K is a measure of the ease of replacement of barium ions in the crystalline phase by radium ions. K will therefore be called the "admittance factor," for the admittance of radium ions to the $BaSO_4$ lattice.

Hoskins and Doerner (1928) found K to be constant over a wide range of concentration of the components of the system. Therefore the ratio of the number of radium ions to the number of barium ions in the crystal is directly proportional to the ratio of the concentration of radium to barium ions in solution over this range of concentrations.

If, in the general case, a_c is the ratio of the ions on the crystal surfaces and a_s the ratio of the ions in solution, then equation (1) can be simplified and rewritten in the form

$$a_c = Ka_s. \qquad (2)$$

The magnitude of K for any such exchange reaction depends on several factors.

(1) The ionic radii and valence similarity of the ions taking part in the reaction. In the $RaSO_4-BaSO_4$ reaction K would be expected to be greater than in the reactions $BeSO_4-BaSO_4$ or $K_2SO_4-BaSO_4$, because the ionic radius of barium, 1.37Å, is more nearly equal to that of radium, 1.52 Å, than that of beryllium, 0.34 Å, and also because the charge on the potassium ion is only one whereas that on the barium ion is two. It is, however, a well known phenomenon of natural silicates that the ionic radius is more critical in determining the possibility of substitution than is valence.

(2) The deformability of the incorporated ions and the ease with which the precipitate is ionized.

(3) The presence in the solution of foreign substances affecting the solubility of the precipitate. Normally this is of minor importance.

(4) The solubility of the accessory element in the liquid phase. This

principle is formulated in the Paneth-Fajans-Hahn adsorption rule: (Kolthoff and Sandell, 1943)

> Those ions whose compounds with the oppositely charged constituent of the lattice are slightly soluble in the solution in question are well adsorbed by the ionic lattice.

Thus, if a compound CA is only slightly soluble, C is more easily adsorbed by the lattice of compound BA than if CA were readily soluble. In the first instance K is larger than in the second.

(5) The temperature at which precipitation occurs. Kolthoff and Noponen (1938) write:

> The heterogeneous mixed crystals of barium and lead sulfate formed on precipitation from acetate medium age very slowly in the supernatant liquid at room temperature but very markedly on digestion at 95° C.

Also, Kolthoff and Eggertsen (1939) write:

> The coprecipitation of chloride with AgBr decreases with increasing temperature during precipitation.

In both of these cases, therefore, an increase of temperature during precipitation caused a decrease in the constant K. It is therefore possible that a similar relation will hold in other cases under similar circumstances.

(6) The pressure in the reacting system. It is to be expected that in most cases the influence of pressure will be slight since the volume changes involved in most liquid-solid exchange reactions are small.

Other factors possibly affect K, but those enumerated above probably represent the most significant ones.

When precipitation is rapid the system may not attain equilibrium during the growth of the crystalline phase. In that case, the amount of foreign material incorporated by the crystalline mass is determined not only by K but also by the rate of crystallization. Kolthoff and Noponen (1938) write:

> The amount of coprecipitation of lead with $BaSO_4$ when the latter is precipitated from acetate solution depends greatly on the speed of addition of precipitant. With very fast addition of the latter the amount of coprecipitation is practically independent of the order of mixing the reagents.

The reverse of this process occurs during rapid crystallization of the precipitates already formed. Kolthoff and Eggertsen (1939) write, when considering the type reaction

$$\underset{\text{(solid)}}{BC} + \underset{\text{(solution)}}{A} \rightleftarrows \underset{\text{(solid)}}{AC} + \underset{\text{(solution)}}{B}$$

> When the reagent C is added slowly to a well-stirred mixture of A and B, the distribution of A (in BC) usually will occur according to the logarithmic expression. (See equation

(10)). However, when the primary precipitate formed is subject to rapid crystallization, the initial distribution of A (and B) will change very rapidly. The primary precipitate, which consists of heterogeneous mixed crystals of BC and AC, will tend to become homogeneous.

As the concentration of the foreign element in a crystalline aggregate is increased, strain is increased in the lattice due to the presence of the foreign element. It is therefore to be expected that, beyond a certain value of the concentration of the foreign ion in the crystal aggregate, the ratio of a_c/a_s will decrease appreciably with the increasing concentration of the foreign element in the liquid phase as this strain effect becomes significant. This is shown graphically in Fig. 1. A point is reached beyond which the amount of foreign element incorporated in the lattice is nearly independent of the concentration of the foreign element in the liquid phase. The maximum concentration of the foreign element in the crystal aggregate will be called A_c.

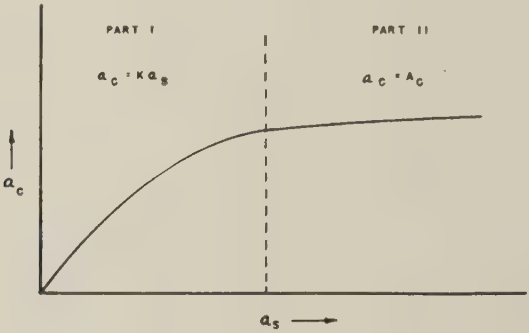

FIG. 1. a_c as a function of a_s.

Incorporation During Crystallization from a Melt

Relations similar to those obtained in aqueous solutions can be observed under quite different conditions. This is illustrated by experiments conducted by McFee (1947) on the incorporation of foreign elements in NaCl crystals during crystallization from a melt. The crystals were grown upward from the base of a cylindrical platinum crucible by lowering the crucible containing the melt of NaCl and the chloride of the foreign element from a hotter to a cooler region of a furnace. The single crystal formed during each run was removed from the crucible and cut into 2 mm. cylinders at right angles to the axis of growth. These cylinders were subsequently analyzed for potassium and copper. The original concentration of potassium was 0.104 atomic per cent, that of copper 0.100 atomic per cent. McFee found that, within experimental error, at these concentrations K was constant at all points in the crystals formed under similar conditions of growth. The curve of Fig. 2 shows that K increased sharply with the rate of growth of the crystal along its long axis. For potassium it was found that K is relatively independent of the rate of growth for rates of growth less than 5 mm. per hour. Above 10 mm. per hour K was found to increase rapidly. If the same is also true for other lattice types and conditions of growth, it can be concluded that in pegmatites K is essentially independent of the rate of crystallization, because the rate of crystallization in pegmatites is probably much slower than 5 mm. per hour.

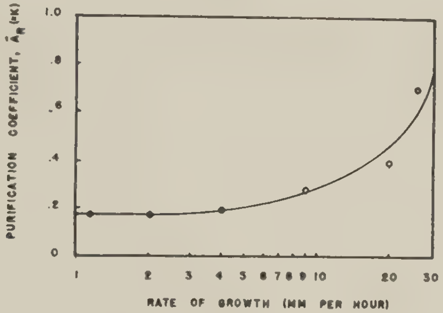

Fig. 2. Taken from R. H. McFee, 1947.

It was stated that in the course of McFee's experiment K was found to be essentially constant under equilibrium conditions. This was only because the amount of the foreign element in the NaCl melt was relatively small. For larger concentrations of foreign elements in the crystallizing melt K deviates from its value for low concentrations. To calculate this deviation the variation in the melting point of the mixture must be determined. A quantitative mathematical and experimental determination of the relative concentration in the melt and in the solid phase of the two constituents of an isomorphous substitution series (complete solid solution) was carried out by Bowen (1913) in his paper on the melting phenomena of the plagioclase feldspars. Bowen's assumptions are contained in the following paragraph:

> For the case of complete solid solution of the type exhibited by the feldspars, we may derive equations expressing the relation between the composition of the liquid and solid in equilibrium at any temperature in the following manner. If both the liquid solutions and the solid solutions are *perfect physical solutions*, i.e., if there is no heat effect or volume change on mixing, then Raoult's law of vapor pressure lowering, and the Clausius equation for the change of vapor pressure with temperature should apply to both components in both phases.

By means of the equations developed by Bowen the concentrations of albite and anorthite in the melt and in the solid phase at temperatures between the melting points of the two components of the plagioclase system were calculated. The liquidus and solidus curves thus obtained closely approximated the values experimentally obtained by Bowen.

From these equations it is possible to derive the following expression for the factor K for the reaction

$$\underset{\text{solid phase}}{\text{(Albite)}} + \underset{\text{melt}}{\text{(Anorthite)}} \rightleftarrows \underset{\text{melt}}{\text{(Albite)}} + \underset{\text{solid phase}}{\text{(Anorthite)}}$$

$$K = e^{L_{Ab}/R(1/T_{Ab}-1/T)-L_{An}/R(1/T_{An}-1/T)} \qquad (3)$$

where

T = temperature (in degrees Kelvin) at which K is being determined
T_{Ab} = melting point of albite (1373°K)
T_{An} = melting point of anorthite (1823°K)
L_{Ab} = latent heat of melting (molal) of albite
L_{An} = latent heat of melting (molal) of anorthite
R = universal gas constant.

Or

$$K = e^{(C/T+D} \qquad (4)$$

where

$$C = \frac{L_{An} - L_{Ab}}{R} \qquad (5)$$

and

$$D = \frac{1}{R}\left(\frac{L_{Ab}}{T_{Ab}} - \frac{L_{An}}{T_{An}}\right). \qquad (6)$$

This means that, if both C and D are positive, K will be largest at the melting point of albite and smallest at the melting point of anorthite. Figure 3 is a plot of K versus T for the plagioclase system, as derived

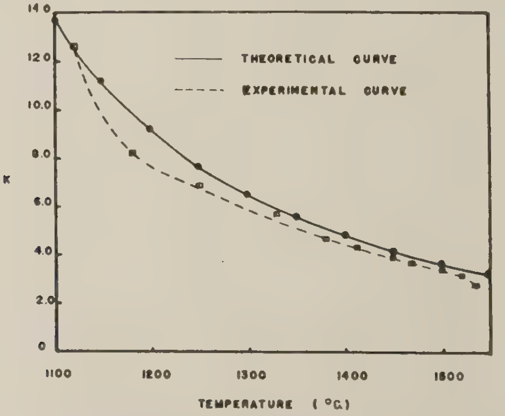

FIG. 3. "K" as a function of the temperature in the plagioclase system, derived from Data of N. L. Bowen, 1913.

from Bowen's diagram, together with the theoretical curve derived from equation (4).

When the percentage of one of the components in a solid-solution pair is small, K will vary but slightly from its value at the freezing point of the major constituent. If, for instance, the percentage of anorthite in an albite-anorthite system is less than one per cent, K for the system of equation (3) would be approximately

$$K \cong e^{L_{Ab}/R(1/T_{Ab}-1/T_{Ab})-L_{An}/R(1/T_{An}-1/T_{Ab})} \tag{7}$$

or

$$K \cong e^{L_{An}/R(1/T_{Ab}-1/T_{An})}. \tag{8}$$

By analogy it should be possible to calculate K for any such isomorphous substitution series provided that the melting points of the components and the latent heat of melting of the minor constituent are known.

It is of interest to note that, when the melting point of the minor constituent is higher than that of the major constituent, K will be greater than 1; if the two constituents melt at the same temperature, K equals 1; and if the melting point of the minor constituent is less than that of the major constituent, K will be less than 1. The heat of melting is always positive.

Values of K larger than the experimentally determined values of McFee were found when equation (8) was used to determine K for the systems $KCl-NaCl$, and $CuCl_2-NaCl$. This indicates that the systems $NaCl-KCl$ and $NaCl-CuCl_2$ do not form ideal isomorphous substitution series.

From McFee's experimental results and the theoretical derivation of K for ideal isomorphous series, it can be stated that the following factors directly affect the magnitude of K for pairs of substances crystallizing from a melt. K is affected by

(1) the melting points of the major and minor constituents,
(2) the latent heat of melting of the major and minor constituents,
(3) the temperature of solidification,
(4) the deviation of the system from that of an ideal isomorphous substitution series,
(5) the deviation from equilibrium during crystallization.

Each of these factors has its counterpart in the factors listed above as affecting K during reactions in aqueous solutions.

From the foregoing discussion it can be concluded that incorporation of foreign elements, even in such widely different processes as the $BaSO_4$-$RaSO_4$ "exchange" in aqueous solution and the incorporation of foreign elements in crystals forming from a melt obey the same general relationships.

Application to Pegmatites

These theoretical considerations are applicable to the study of pegmatites because field investigation by Schaller (1925), Page (personal communication), Jahns (1946), and others indicate that in the cooling history of many pegmatites the pegmatite liquid passed through a stage corresponding to a crystallizing melt (magmatic stage) and also through a stage corresponding to an aqueous solution (hydrothermal stage). It has been shown above that incorporation of accessory elements into crystal lattices obeys similar laws under both magmatic and hydrothermal conditions. Consequently it can be assumed that under conditions intermediate between these two extremes the incorporation of foreign elements will obey the same laws.

THE DISTRIBUTION OF ACCESSORY ELEMENTS IN PEGMATITES AS A FUNCTION OF THE DISTANCE FROM THE WALL ROCK-PEGMATITE CONTACT

A. Only One Lattice Type Present in the Pegmatite

Mathematical expressions will be derived to express the concentration of accessory elements in a pegmatite as a function of the distance from the wall rock contact. Two cases can be distinguished. The first corresponds to the concentration relation expressed by Part I of Fig. 1 (linear conditions); the second case corresponds to the concentration relation expressed by Part II of Fig. 1 (saturation conditions).

Linear Conditions. If linear conditions prevail, the incorporation of the accessory element is controlled by the equation

$$a_c = Ka_s.$$

Let us consider again the reaction

$$BaSO_4 + RaCl_2 \rightleftarrows RaSO_4 + BaCl_2$$

in which the concentration of the products and reactants is controlled by equation (1).

$$\frac{\text{no. of Ra}^{++}\text{ on surface}}{\text{no. of Ba}^{++}\text{ on surface}} = K\frac{[\text{Ra}^{++}]\text{ in solution}}{[\text{Ba}^{++}]\text{ in solution}}.$$

It was noted that when H_2SO_4 is added to a solution of $BaCl_2$ and $RaCl_2$, the concentrations of $BaCl_2$, $RaCl_2$, $BaSO_4$, and $RaSO_4$ are controlled by the equations

$$BaCl_2 + H_2SO_4 \rightleftarrows BaSO_4 + 2HCl$$

and

$$BaSO_4 + RaCl_2 \rightleftarrows BaCl_2 + RaSO_4$$

provided that the solubility product constant of $RaSO_4$ is not exceeded.

In Table 1 the concentrations of reactants and products at different stages of precipitation are defined.

TABLE 1

CONCENTRATION OF COMPONENTS IN $RaSO_4$-$BaSO_4$ SYSTEM

Component	Concentration before addition of H_2SO_4	Concentration after a small volume of H_2SO_4 has been added	Final Concentration
$BaSO_4$	0	*$\Delta[BaSO_4]$	$[BaSO_4]_F$
$RaSO_4$	0	$\Delta[RaSO_4]$	$[RaSO_4]_F$
$BaCl_2$	$[BaCl_2]_0$	$([BaCl_2]_0 - \Delta[BaSO_4])$	$[BaCl_2]_F$
$RaCl_2$	$[RaCl_2]_0$	$([RaCl_2]_0 - \Delta[RaSO_4])$	$[RaCl_2]_F$

* The symbol Δ represents a small increment.

The change in the $BaCl_2$ concentration, $\Delta[BaCl_2]$, is equal in magnitude to the change in concentration of $BaSO_4$, $\Delta[BaSO_4]$. Similarly, the change in the $RaCl_2$ concentration, $\Delta[RaCl_2]$, is equal in magnitude to the change in concentration of $RaSO_4$, $\Delta[RaSO_4]$. Mathematically expressed, these relations are

$$|\Delta[BaCl_2]| = |\Delta[BaSO_4]|$$
$$|\Delta[RaCl_2]| = |\Delta[RaSO_4]|.$$

When these relations are substituted into equation (1), that equation becomes

$$\frac{\Delta[RaCl_2]}{[RaCl_2]_0 - \Delta\,|[RaCl_2]} = K\frac{\Delta[BaCl_2]}{[BaCl_2]_0 - \Delta[BaCl_2]}. \tag{9}$$

From this expression the concentration of $RaSO_4$ can be calculated in terms of the concentration of the other components after a volume of H_2SO_4 has been added such that the concentration of $BaCl_2$ is $[BaCl_2]_F$. The effect of adding H_2SO_4 on the components in expression (3) must then be summed. This can be done by integrating expression (3) from the initial to the final state of the system. Expression (3) then becomes

$$\log\frac{[RaCl_2]_F}{[RaCl_2]_0} = K\log\frac{[BaCl_2]_F}{[BaCl_2]_0}. \tag{10}$$

Equation (10) can be rearranged to the form

$$[RaCl_2]_F = [RaCl_2]_0\left(\frac{[BaCl_2]_F}{[BaCl_2]_0}\right)^K. \tag{11}$$

At equilibrium in the final state equation (1) is valid. Therefore

$$\frac{[RaSO_4]_F}{[RaCl_2]_F} = K\frac{[BaSO_4]_F}{[BaCl_2]_F}. \tag{12}$$

Thus the final concentration of $RaSO_4$ will be

$$[RaSO_4]_F = [RaCl_2]_F \cdot K \cdot \frac{[BaSO_4]_F}{[BaCl_2]_F} . \qquad (13)$$

The substitution of expression (11) for $[RaCl_2]_F$ in this equation yields

$$[RaSO_4]_F = K[RaCl_2]_0 \frac{[BaSO_4]_F}{[BaCl_2]_F} \left(\frac{[BaCl_2]_F}{[BaCl_2]_0} \right)^K . \qquad (14)$$

When this expression is rearranged, it becomes

$$[RaSO_4]_F = K[RaCl_2]_0 \frac{[BaSO_4]_F}{[BaCl_2]_0} \left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1} .$$

If both sides are divided by $[BaSO_4]_F$, then

$$\frac{[RaSO_4]_F}{[BaSO_4]_F} = K \frac{[RaCl_2]_0}{[BaCl_2]_0} \left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1} . \qquad (15$$

By definition,

$$\frac{[RaSO_4]}{[BaSO_4]} = a$$

and

$$\frac{[RaCl_2]}{[BaCl_2]} = a_s .$$

Therefore equation (15) can be rewritten in the form

$$a_{c_F} = K \cdot a_{s_{0,1}} \left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1*} . \qquad (16)$$

This means that the concentration of Ra in the precipitate is:

(1) linearly related to the original concentration of $RaCl_2$ in solution;
(2) linearly related to the admittance factor, K;
(3) related to the fraction of barium sulfate precipitated by the expression

$$\left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1} .$$

Let the molar volume of $BaSO_4$ be defined as F_{BaSO_4} and the molar volume of $BaCl_2$ as F_{BaCl_2}. Also, let

v = final volume of $BaSO_4$
V = original volume of $BaCl_2$.

It follows that

$$\frac{[BaSO_4]_F}{[BaCl_2]_0} = \frac{v/F_{BaSO_4}}{V/F_{BaCl_2}} . \qquad (17)$$

In a pegmatite of one lattice type the solid phase will correspond to the precipitate of $BaSO_4$ and the liquid phase to $BaCl_2$. Let the molar volume of the solid phase be F_c and the molar volume of the liquid phase be F_s; then equation (16) can be written in the form

---

* The subscript 0,1 is used for the sake of consistency with equations 24 ff.

$$a_{c_F} = Ka_{s_{0,1}}\left(1 - \frac{vF_s}{VF_c}\right)^{K-1}. \tag{18}$$

In most cases the difference between F_s and F_c is negligible. Then equation (18) reduces to the form

$$a_{c_F} = Ka_{s_{0,1}}\left(1 - \frac{v}{V}\right)^{K-1}. \tag{19}$$

McFee (1947) has derived expression (19) from the relationship

$$a_c = Ka_s$$

in a somewhat different manner in his work on the distribution of accessory elements in NaCl crystals.

In Fig. 4, a_c is plotted as a function of v/V for various values of K at $a_{s_{0,1}} = 1$, and $F_s = F_c$. Three general cases can be distinguished.

(1) K less than 1. In this case, a_c increases with v/V; i.e., the concentration of the foreign element increases with continued crystallization.

(2) K equals 1. In this case a_c is independent of the state of crystallization; i.e., the foreign material will be uniformly distributed throughout the crystallized mass.

(3) K is greater than 1. In this case the concentration of the foreign element decreases with progressing crystallization.

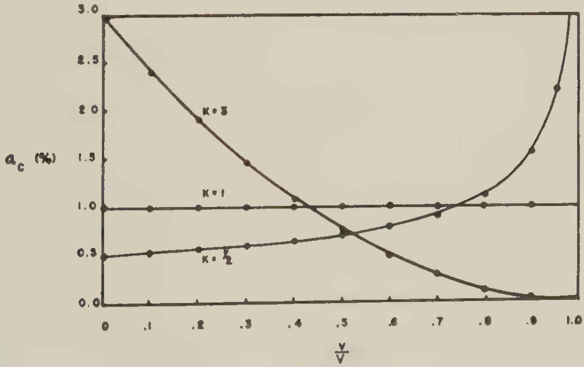

FIG. 4. a_c as a function of v/V for values of "K" greater than, equal to, and less than one.

In nature it is to be expected that cases (1) and (3) would be most widely represented since case (2) merely represents a boundary condition between them. According to Page (personal communication) the "mineralizers" in South Dakota pegmatites would fall into class (1) because many "mineralizers," such as lithium salts, appear to be successively enriched in the rest-liquid of pegmatites. That the alkalies in general tend to be concentrated in the rest-liquids is indicated in the report on the Strickland-Cramer deposit of Connecticut by Jenks (1935). In listing the optical data gathered for six specimens of beryl from different zones of the pegmatite, Jenks finds that the index of refraction of beryl is higher at low temperatures than at high temperatures of deposition. A definite relation between refractive index and the percentage of alkalies has been established by Winchell (1933). On this basis Jenks concludes that the percentage of alkalies in the beryl formed during the late stages of crystallization is greater than that formed during the initial stages of cooling of the pegmatite.

An example of the third case ($K > 1$) has already been cited in the case of the plagioclase system. Since anorthite melts at a higher temperature than albite,

$$\left(\frac{1}{T_{Ab}} - \frac{1}{T_{An}}\right)$$

will be positive. Therefore K will be greater than unity. Page (personal communication) has found that in the pegmatites of the Keystone District of South Dakota the indices of refraction of plagioclase feldspars in numerous pegmatites show that the contained plagioclase is either uniform in composition from wall to wall or its anorthite content decreases from the wall to the core, and that these changes in the anorthite content of plagioclase in the pegmatite are analogous to the normal variation of plagioclase composition in igneous rocks.

Saturation Conditions. Under saturation conditions Part II of the curve in Fig. 1 is applicable to the problem. In this part of Fig. 1, a_c is independent of a_s. Therefore, if the saturation concentration of the foreign material is A_c, it follows that after a volume "v" has crystallized from the melt or solution a quantity $A_c v$ of the foreign constituent has been incorporated in the crystalline mass, and the concentration of the foreign material in the solution or magma at this point will be

$$\frac{a_{s_{0,1}}V - A_c v}{V - v}. \tag{20}$$

The concentration of the foreign constituent in the crystalline mass will be independent of the volume, v, which has crystallized out; i.e., no variation in the percentage of the foreign element from wall to wall will be noticed. In this sense, therefore, the distribution of the foreign constituent will be the same as in the case in which $K = 1$ and in which a_c and a_s are linearly related. It may therefore be difficult to determine which of the two situations was responsible for the distribution. A laboratory determination of K for such an incorporation reaction may be necessary to solve the problem.

If we consider an incorporation reaction in which the complete curve of Fig. 1 graphically depicts the relationship between a_c and a_s, it is possible to determine the distribution of the accessory element, and the effect of K and A_c on its distribution. When K is greater than or equal to unity the saturation region will not be reached and the distribution of the accessory element will follow the appropriate curve in Fig. 4. When K is less than unity, the distribution of the accessory element will follow the curve for $K<1$ in Fig. 4, until a_s reaches the value A_c/K. At that point the saturation region of the main constituent with respect to the accessory element is reached. For material crystallizing out at a later stage, a_c will be equal to the saturation concentration, A_c, as indicated in Fig. 5. The larger A_c is for the substitution reaction, the greater will be the volume of the pegmatite for which the distribution of the accessory is controlled by equation (2).

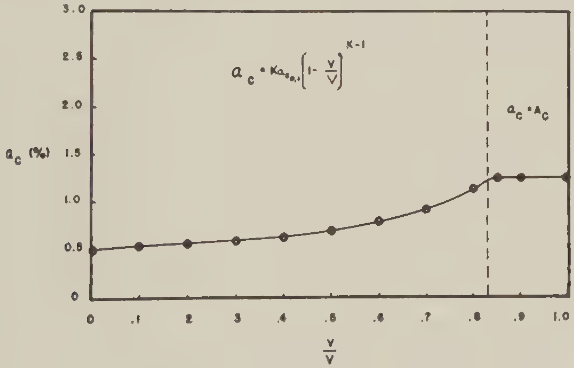

FIG. 5. a_c as a function of v/V before and after entering the saturation region. $K=0.5$; $a_{s_{0,1}}=1.0$; $a_c=1.25$.

B. *More Than One Lattice Type Present*

In the past paragraphs expressions for the distribution of an accessory element as a function of the amount of material crystallized were developed for the case in which only one lattice type is present in the pegmatite. It is now of interest to investigate the distribution of accessory elements when more than one lattice type is present, as is usually the case in pegmatites. Two situations are possible: either the zones of the pegmatite are monomineralic, or they contain more than one lattice type. Both possibilities are to be discussed.

Monomineralic Zones. It will first be assumed (1) that the cooling body solidifies from the wall-zone inward, the core being the last portion of the body to solidify, and (2) that no disturbing factors such as addition or escape of material, convection, shattering, veining, or replacement affect the cooling history of the pegmatite, and that the pegmatite cools slowly enough so that diffusion gradients do not affect the nature of the solutions at the boundary of the crystalline phase. With these assumptions, the theoretical distribution of accessory elements can be calculated for the following cases:

(1) The relation

$$a_c = Ka_s$$

is true throughout the crystallization history of the pegmatite.

(2) The relation

$$a_c = A_c$$

is true throughout the crystallization history of the pegmatite.

(3) The above relations apply to the crystallization process at different stages during the solidification of the pegmatite liquid.

(1) The distribution equation for an accessory element for which the equation

$$a_c = Ka_s$$

describes the distribution of the element in the solid and liquid phase is to be derived.

Let v_l be the total volume of the constituents of lattice type 1 in the melt. Let a_{c_1} be a_c for the foreign element in lattice type 1. Furthermore, let $a_{s_{1,2}}$ be the ratio of the quantity of the foreign element in the melt to the concentration of the main constituent of lattice type 2 in the melt after type 1 has just finished crystallizing out and type 2 is just beginning to solidify.

$$a_{s_{1,2}} = \frac{\text{[foreign element] in melt}}{\text{[main constituent of lattice type 2] in melt}}. \tag{21}$$

Further, let C_f be the original concentration of the foreign element in the melt. Therefore, since the original volume of the melt was V, the total number of moles of the foreign element in the pegmatite is $C_f \cdot V$. The volume of the foreign element incorporated by a small volume, Δv, of lattice type 1 will be

$$\frac{\text{[foreign element] in solid phase}_1}{\text{([foreign element] + [main constituent]) in solid phase}_1} \cdot \Delta v.$$

When the percentage of the foreign element is small, this expression is approximately equal to

$$\frac{\text{[foreign element] in solid phase}_1}{\text{[main constituent] in solid phase}_1} \cdot \Delta v.$$

But this by definition is $a_{c_1} \cdot \Delta v$.

The total quantity in moles of the foreign element incorporated in lattice type 1 will be the sum of $a_{c_1} \cdot \Delta v$ over the volume of lattice type 1 which will have crystallized out before lattice type 2 starts to solidify. This volume will not be exactly equal to v_1, the total volume of the constituents of lattice type 1 in the melt, since the solubility of the solid phase in the liquid phase is never zero. The volume of lattice type 1 which has crystallized out when lattice type 2 begins to solidify will be called v_1'.* The total quantity in moles of the foreign element incorporated in lattice type 1 will therefore be

$$\frac{1}{F_f} \int_0^{v_1'} a_{c_1} dv$$

where F_f is the molar volume of the foreign element.

The quantity of the foreign element remaining in the melt after the crystallization of lattice type 1 will be the original quantity minus the amount removed by incorporation into lattice type 1. Therefore the number of moles of the foreign element remaining in the melt will be

$$C_f V - \frac{1}{F_f} \int_0^{v_1'} a_{c_1} dv. \tag{22}$$

Let C_2 be the original molar concentration of the major component of lattice type 2 in the melt. The number of moles of the component of lattice type 2 present in the melt before the commencement of crystallization of lattice type 2 is therefore

$$C_2 \cdot V. \tag{23}$$

Substituting expressions (22) and (23) into expression (21), $a_{s_{1,2}}$ becomes

$$a_{s_{1,2}} = \frac{C_f}{C_2} - \frac{1}{F_f C_2 V} \int_0^{v_1'} a_{c_1} dv. \tag{24}$$

In this expression

$$a_{c_1} = a_{s_{0,1}} \cdot K_1 \left(1 - \frac{v}{v_1}\right)^{K_1 - 1} \tag{25}$$

where

$a_{s_{0,1}}$ = ratio of moles of foreign element to moles of main constituent of lattice type 1 at start of crystallization.

K_1 = admittance factor of the foreign element in question to lattice type 1

$F_{c_1} \cong F_{s_1}$.

By analogy, $a_{s_{2,3}}$, defined as the ratio of the quantity of the foreign material to that of the main constituent of lattice type 3 in the melt at the start of the solidification of lattice type 3, can be written in the form

---

* It follows from equation (19) that if v_1' were equal to v_1, all of the foreign element would be incorporated into lattice type 1 irrespective of the value of K for the element in lattice type 1. This can be shown by integrating the expression a_{c_1} dv between the limits 0 and v_1.

$$a_{s_{2,3}} = \frac{C_f}{C_3} - \frac{1}{F_f C_3 V}\left[\int_0^{v_1'} a_{c_1} dv + \int_0^{v_2'} a_{c_2} dv\right] \tag{26}$$

v_2' is defined as the volume of lattice type 2 which has crystallized out before lattice type 3 has started to solidify. The quantity a_{c_2} is defined by the expression

$$a_{c_2} = a_{s_{1,2}} \cdot K_2 \left[1 - \frac{v}{v_2}\right]^{K_2 - 1} \tag{27}$$

where

K_2 = admittance factor of the foreign element in question to lattice type 2

and

$$F_{c_2} \cong F_{s_2}.$$

By analogy to expressions (24) and (26), $a_{s_{(n),(n+1)}}$ will be

$$a_{s_{(n),(n+1)}} = \frac{C_f}{C_{(n+1)}} - \frac{1}{F_f C_{(n+1)}} \sum_{i=0}^{i=n} \int_0^{v_1'} a_{c_i} dv. \tag{28}$$

In this expression

$C_{(n+1)}$ = concentration of lattice type $(n+1)$ in the original pegmatite melt (or solution)

a_{c_i} = ratio of the concentration of the foreign element to the concentration of the main constituent in the crystalline phase of lattice type

$$a_{c_i} = a_{s_{(i-1),(i)}} K_i \left[1 - \frac{v}{v_i}\right]^{K_i - 1} \tag{29}$$

and

$$F_{c_i} \cong F_{s_i}.$$

In a similar manner the concentration of a foreign element at the interface of any two lattice types of the pegmatite can be calculated.

To determine the concentration of a foreign element in a lattice type after a certain portion of that lattice type has crystallized, equation (29) must be modified. For instance, if this concentration is to be determined after one half of lattice type $(n+1)$ has crystallized out, then a_c at that point will be

$$a_c = a_{s_{(n),(n+1)}} \cdot K_{(n+1)} (\tfrac{1}{2})^{K_{(n+1)} - 1}. \tag{30}$$

Since $a_s = a_c/K$, the ratio of the concentration of the foreign element to that of the main constituent in the melt at this point in the process of crystallization will be

$$a_s = a_{s_{(n),(n+1)}} (\tfrac{1}{2})^{K_{(n+1)} - 1}. \tag{31}$$

A similar procedure can be applied to find a_c and a_s at other points not at the interface between lattice types.

(2) It is possible to calculate also a_c and a_s at the same point, e.g., after one half of lattice type $(n+1)$ has crystallized out, for the case in which the saturation region of all the lattice types 1 to $(n+1)$ with respect to the foreign material in question is maintained. When half of lattice type

(n+1) has crystallized out,

$$a_c = A_c \tag{32}$$

and

$$a_s = \frac{C_fV - \frac{1}{F_f}\sum_{i=0}^{i=n} A_i v_i{}' - \frac{A_{c(n+1)}V_{(n+1)}}{2F_f}}{\frac{C_{(n+1)}V}{2}}. \tag{33}$$

Under these conditions, the residual solutions will be enriched in the foreign constituent.

(3) A third case is possible. The distribution of lattice types may be such that at one point in the crystallization process the concentration of the foreign material is such that a_c and a_s are proportional, while at another stage of crystallization the saturation region of a lattice with respect to the foreign constituent is maintained. Under such conditions the equations derived above no longer apply for the whole crystallizing body. It will then be necessary to investigate the distribution of foreign elements in each pegmatite zone separately.

More Than One Lattice Type Per Zone. In many pegmatites more than one mineral type is present in each zone. Intimate mixtures of lepidolite and cleavelandite, or spodumene and quartz, and of many other constituents have been described. Such mixtures require that the equations developed above be modified somewhat. Let there be two lattice types, 1 and 2, intimately associated at a certain point in the pegmatite. Then

$$a_{c_1} = a_sK_1 \tag{34}$$

and

$$a_{c_2} = a_sK_2 \tag{35}$$

provided that the concentrations are such that a_s and a_c are linearly related in both lattice types. The amount of foreign material removed from the solution or magma during the crystallization of a volume v in this area will be

$$\int_0^v (p_1a_{c_1} + p_2a_{c_2})dv$$

where p_1 and p_2 are the fractions of lattice types 1 and 2 respectively. If, therefore, $C_f/(C_1+C_2)$ is substituted for $a_{s_{0\,1}}$, the expression $(p_1a_{c_1}+p_2a_{c_2})$ is substituted for a_c in the original derivation, and $(p_1K_1+p_2K_2)$ is substituted for K, a_c can be determined as a function of v/V. Thus

$$p_1a_{c_1} + p_2a_{c_2} = \frac{C_f}{C_1 + C_2}(p_1K_1 + p_2K_2)\left(1 - \frac{v}{V}\right)^{(p_1K_1+p_2K_2-1)}. \tag{36}$$

when $F_c \cong F_s$. Analogous expressions can be derived for the case in which a larger number of lattice types are present in a given zone of the cooling pegmatite.

When the saturation conditions are maintained throughout the crystallization of lattice types 1 and 2 under the same conditions as above, the equations for a_{c_1} and a_{c_2} will be

$$a_{c_1} = A_c$$

and

$$a_{c_2} = A_c$$

respectively.

It is of interest to apply the above formulae to a specific case. Let the pegmatite under consideration consist of two lattice types, 1 and 2, which crystallize out simultaneously but are crystallographically incompatible. Let one accessory element be present in the original melt, in a concentration of one per cent, and let the admittance factor of this accessory element be 0.5 for lattice type 1 and 2.0 for lattice type 2. Let the ratio of the concentration of lattice type 1 to lattice type 2 be one to three. In that case

$$p_1 = 0.25$$
$$p_2 = 0.75.$$

Also, let $F_c \cong F_s$ for both lattice types. When the above values are substituted in equation (36) the following expression is obtained.

$$0.25a_{c_1} + 0.75a_{c_2} = 0.01(1.625)\left(1 - \frac{v}{V}\right)^{(0.625)} \tag{37}$$

or

$$0.25a_{c_1} + 0.75a_{c_2} = 0.01625\left(1 - \frac{v}{V}\right)^{(0.625)}. \tag{38}$$

From equations (34) and (35) it is known that

$$a_{c_2} = a_{c_1} \cdot \frac{K_2}{K_1}.$$

Therefore

$$a_{c_2} = a_{c_1} \cdot 4.0.$$

When this value for a_{c_2} is substituted into equation (38), the following value of a_{c_1} is obtained:

$$a_{c_1} = \frac{0.01625}{3.25}\left(1 - \frac{v}{V}\right)^{(0.625)}$$

or

$$a_{c_1} = 0.0050\left(1 - \frac{v}{V}\right)^{(0.625)}. \tag{39}$$

Also

$$a_{c_2} = 0.020\left(1 - \frac{v}{V}\right)^{(0.625)}. \tag{40}$$

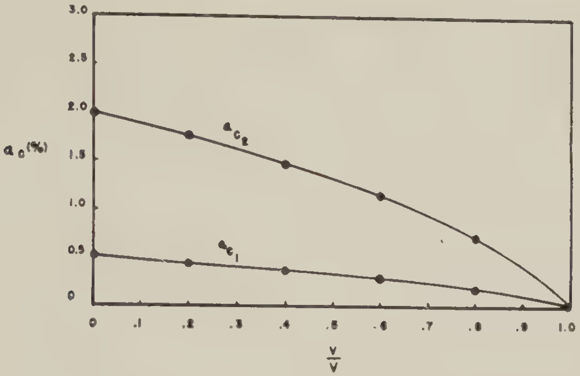

FIG. 6. a_{c_1} and a_{c_2} as functions of v/V.

TABLE 2. CALCULATION OF a_{c_1} AND a_{c_2} AS FUNCTIONS OF v/V

(v/V)	(1−v/V)	$(1-v/V)^{(0.625)}$	a_{c_1}	a_{c_2}
0	1.0	1.00	0.500%	2.00%
0.20	0.8	0.870	0.435	1.74
0.40	0.6	0.725	0.362	1.45
0.60	0.4	0.565	0.287	1.13
0.80	0.2	0.366	0.183	0.73
1.00	0	0	0	0

In Table 2 a_{c_1} and a_{c_2} are recorded as functions of v/V. In Fig. 6 the data of Table 2 is graphically presented.

It is of interest to note that, whereas $K<1$ for the lattice type 1, the concentration of the accessory in this lattice type decreases rather than increases with increasing v/V. This is due to the presence of lattice type 2 in such quantities that for the combination of lattice types 1 and 2 K is greater than 1.

If the concentration of lattice type 1 in the crystalline mass were such that for the combination of 1 and 2 $K<1$, then the concentration of the foreign constituent would increase in both lattice types as the processes of crystallization proceeded.

The assumption made at the beginning of this section about the direction of crystallization in pegmatites is not always warranted. Not in all cases does crystallization start at the wall of the pegmatite and proceed toward the center of the body. Page (personal communication) states that "many of the larger pegmatites of New England contain pods of coarse quartz, perthite, plagioclase, muscovite, beryl, and other minerals in various combinations and proportions. The sequence of lithologic units outward from any given pod is commonly consistent for a particular pegmatite." In such a case the volume of pegmatite crystallized out, v, must be calculated from the center of the pod outward rather than from the wall of the body inward as in pegmatites where zones are concentrically arranged around the core.

By means of the expressions developed in the foregoing sections it should be possible to calculate the distribution of elements foreign to the lattice types of pegmatites for a great variety of these bodies, provided the following data are available.

(1) The total volume and shape of the pegmatite.
(2) The concentration of the foreign element and of the constituents of the various lattice types in the original melt.
(3) The volume of each lattice type which crystallizes out before the next lattice type begins to solidify.
(4) The value of the admittance factor, K, for the foreign element for each lattice type as a function of a_c.
(5) The molar volume of the foreign element and of the lattice types of the pegmatite both in the liquid and solid state.
(6) The fraction of each lattice type in the various zones of the pegmatite.
(7) The disturbing factors in the cooling history of the pegmatite.

THE EFFECT OF DISTURBING FACTORS IN THE COOLING HISTORY OF A PEGMATITE ON THE DISTRIBUTION OF ACCESSORY ELEMENTS

In the above distribution treatment several assumptions were made about the absence of disturbing factors in the process of crystallization in pegmatites. Some of these assumptions may not be valid in specific cases of pegmatite crystallization, and therefore should be discussed in their bearing on the foregoing derivations.

(1) One of these assumptions was that the material present in the pegmatite at the beginning of crystallization is retained by the pegmatite during solidification, and is finally incorporated in the material crystallizing in the last stages of cooling. This is not the case when, as has been shown in some instances, some of the original constitutents escape from the solidifying mass, and enter the surrounding rock. This tendency to escape from the rest liquid is especially true of the volatile constituents of the pegmatite mass. For these constituents either $K < 1$ in most of the lattice types of the cooling mass, or their concentration is such that the saturation region of the $a_c = a_s$ curve is occupied during the cooling process.

In either case, the effect of the escape of the volatile constituents on their concentration in lattice types crystallizing after their escape, depends on the equations controlling the concentration of the volatile constituents in these lattice types. If the concentration is controlled by the equation

$$a_{c_n} = K_n a_{s_n}$$

then the escape of a volume of the volatile constituents, such that a_{c_n} is decreased by Δa_{s_n}, will decrease the concentration of the constituent in lattice type n by the amount $K_n \cdot \Delta a_{s_n}$; i.e.,

$$\Delta a_{c_n} = K \Delta a_{s_n}. \qquad (41)$$

On the other hand, if the concentration of the volatile constituents in the melt, after the escape of some of the volatile constituents, is such that $a_{c_n} = A_{c_n}$, then the escape of volatile constituents will inappreciably alter their concentration in lattice type n, unless by this escape the region in which a_{c_n} is proportional to a_{s_n} is entered.

(2) Convection currents might be set up in pegmatites by uneven cooling. This would result in non-uniform crystallization and composition at different parts of the pegmatite body.

(3) Shattering and veining of pegmatites have been reported from a number of districts (Cameron, Jahns, McNair, Page—to be published). In many instances cracks appear in the pegmatite before final consolidation. In that case the residual liquids fill the gaps created in the wall. Subsequent cooling may then lead to deposition of either mono- or polymineralic veinfilling. Zoning parallel to the walls of the cracks has been reported. Such zones correspond to those developed in the main body of the pegmatite after the formation of the veins. It is to be expected that the distribution of accessory elements in the vein-filling material will be similar to the distribution in the corresponding zones of the main body.

When the vein-filling material reacts with crystalline pegmatite, replacement phenomena appear. This is a special case of the general problem of replacement treated below.

(4) Another assumption made in the derivation of the distribution equations was that interaction of the residual liquid with the crystal mass already formed is negligible. This situation might not prevail when:

(a) the increase of pressure due to the concentration of volatile constituents in the residual liquids causes corrosion of the crystalline phase by the residual liquids; or

(b) additional material added in some way to the rest liquids endows the rest liquids with sucb corrosive properties. Additional material of this nature might be added from the source of the original pegmatite melt through fissures in the pegmatite and country rock developed subsequent to partial solidification of the pegmatite

The effect of interaction of the rest liquids with the crystallized portion of the pegmatite on the distribution equations developed in earlier sections of this paper may be considerable. It is to be expected that interaction would take place between the material crystallizing in newly formed fissures and the earlier minerals surrounding these fissures. The formation of pseudomorphs of earlier minerals by the corrosive action of the rest liquids indicates that the changes due to such interaction may be profound. It is therefore to be expected that in a pegmatite in which there has been considerable interaction of the rest liquids and the crystalline phase, the plot of concentration of foreign elements versus distance from the wall-rock pegmatite contact would not follow the equations previously developed. It is also to be expected that the degree of deviation from these relations will be proportional to the amount of interaction between the rest liquids and the crystalline phase.

(5) Finally, crystallization may at times be so rapid that the rate of diffusion of materials from the central part of the pegmatite affects the composition of the pegmatite liquids at the liquid-solid boundary. Since the cooling time of pegmatites must have been considerable, it is probable that the effect of the diffusion gradient on the distribution of accessory elements in the solid phase was in most cases negligible. However, this can only be proved when data on the rate of cooling, viscosity, and composition of the pegmatitic liquids is more complete.

General Summary and Application

The means of incorporating an accessory element in a crystal mass have been discussed and theoretical relations between a_s and a_c (the ratio of the concentration of the accessory to the main constituent in the liquid and in the solid phase), have been formulated. These theoretical relationships were first applied to the case of a crystallizing pegmatite containing only one type of lattice, then to one containing more than one type of lattice in zonal arrangement, and subsequently to a mass containing several lattice types somewhat more randomly arranged within the crystallizing mass. For each of these cases, the distribution of accessories was discussed. Two conditions were discerned: (1) a_c proportional to a_s ("linear" conditions), and (2) a_c independent of a_s ("saturation" conditions). Finally, some of the assumptions made in the derivation of these relationships were investigated and an attempt was made to ascertain the effect of relaxing some of the conditions imposed by these assumptions.

These theoretical relationships must now be tested by evidence gathered in the field and by suitable supporting laboratory experiments. The field evidence needed can be obtained by cross-sectional sampling of pegmatites, the cooling history of which can be at least partially ascertained from field relationships. A clearly zoned pegmatite in which replacement phenomena are relatively unimportant would be the most desirable object of study. Adequate laboratory analyses of rock specimens should then yield data to support or invalidate the expressions derived above for a_c as a function of v/V.

Laboratory experiments on the incorporation of accessories in crystal masses, similar to the experiments carried out by McFee (1947), will serve to determine the necessary data on the admittance of various lattices for accessory elements under different conditions of crystallization.

Work is in progress in this laboratory in order to obtain necessary data for the evaluation of the theory. Preliminary results are encouraging.

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The writers assume all responsibility for the views expressed in this study.

Since this paper was written, the article by H. Neumann (1948) has come to the authors' attention. The problem treated by Neumann involves the distribution of the original constituents of the magma between the molten and the fluid phases developed during the process of solidification. This problem is similar to the main question treated above, i.e., the distribution of the constituents of the pegmatitic fluids between the solid and liquid state after emplacement. It is of note that the fundamental equations are the same in both cases.

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CRYSTAL CHEMICAL RELATIONS IN INORGANIC PIEZOELECTRIC MATERIALS

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ABSTRACT

An attempt is made to establish a relation between the structure and the piezoelectric activity of a number of inorganic salts. The possession of activity by a salt appears to depend in many cases on the presence of an asymmetric radical and is further influenced by the nature of the cationic environment of this radical.

Increased interest in specialized electronic gear has resulted in a renewed search for new synthetic piezoelectric materials. The wartime production of large single crystals of $NH_4H_2PO_4$ is a notable example.

Piezoelectric activity depends on the absence of a center of symmetry in the crystal structure of a compound. Thus, when it is definitely known that a compound crystallizes in one of 20 of the possible 32 crystal classes, piezoelectric response can be assumed without testing.[1] The magnitude of the effect, however, cannot be so simply predicted.

Crystal symmetry data, moreover, are thoroughly reliable for relatively few materials. A large proportion of the older data which assigned the crystal to a class on the basis of morphological observations is not correct; even with modern x-ray data, determination of the crystal class is often very difficult. Where the final determination depends on the presence or absence of a center of symmetry, the decision can often be made only on the basis of a test for piezoelectricity. A thorough search of the literature resulted in a rather long list of materials that had been tested, and also revealed many discrepancies and many results which, on the basis of later reliable symmetry data, were obviously incorrect. Accordingly, the Crystal Section of the Naval Research Laboratory has undertaken a comprehensive laboratory survey of piezoelectric materials and has completed the testing of all the likely water-soluble inorganic compounds which were obtainable in the necessary form. From a list of 400 potentially active compounds, 155 compounds were measured, and the remainder eliminated for lack of practical value and because of difficulty of preparation. Sixty-six active salts were reported in this study.[2] Thirtyone of the compounds tested were inactive despite the fact that the literature either reported them as belonging in active crystal classes or disagreed as to the symmetry class.

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[1] Wooster, W. A., "Crystal Physics," Cambridge Press (1938) pp. 217. Wooster makes the following statement of this point: "Where a piezoelectric effect cannot be detected, even though the external development shows a center of symmetry to be absent, the piezoelectric observation does not affect the assignment of the crystal to its symmetry class."

[2] Egli, P., A survey of inorganic piezoelectric materials: *Am. Mineral.*, **33**, 623–634 (1948).

The purpose of this paper is not to present the revised data but to summarize some of the general relations observed which add additional information on the structural relationships between various types of ions in inorganic chemicals.

The device[3] used to detect piezoelectricity is a modification of the circuit originally used by Giebe and Scheibe in which activity is excited in the crystal sample by the electric field from a high-frequency oscillator. The frequency of the oscillator is varied rapidly and as various resonances are excited in the crystal, the modulation between the frequency of the crystal vibration and the changing oscillator frequency causes clicks that are audible in earphones. The Naval Research Laboratory design of this device has proved highly reliable and free of spurious responses so that clicks over a range of frequencies constitute a positive indication of piezoelectric activity. A negative response is less certain since several conditions must be satisfied before activity may be detected. For instance, high conductivity or poor elastic properties may interfere with detection of piezoelectricity, though they usually result in a sizzling noise which is readily identified. In inorganic materials conductivity is rarely a factor except in oxides and sulfides, and no case was found in which poor elastic properties were a problem. The crystal specimen must also, of course, be of such a size that it will have a resonance within the range of the oscillator, which has a top frequency of 10 Mc. In general, well formed crystals as small as +100-mesh could be tested reliably. As there is relatively little variation in conductivity and elastic properties among inorganic materials, the strength of the click provides an approximate quantitative measure of the effective strength of the piezoelectric response.

Structural Relations

The correlation of piezoelectric activity with structure does not appear to be a simple matter. Given a favorable symmetry structure for piezoelectric response, the magnitude of the effect depends in a complex way on the difference in strength of the anion and cation. The strongly active compounds usually contain cations of the alkali metals, hydrogen or ammonium.

Wooster[1] has listed some of the general crystal-chemical relationships found to exist in piezoelectric inorganic salts. These relationships involved a consideration of the constituent anion and cation groups in the lattice. In general, it is true that asymmetry in either a complex anion or cation may influence the whole lattice in favor of piezoelectricity, but it is also often necessary to consider the interaction of the two groups as they affect the over-all symmetry of the crystal. These interacting structural relationships can be formulated as follows:

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[3] Stokes, R. G., An improved apparatus for detecting piezoelectricity: *Am. Mineral.*, **32,** 670–679 (1947).

1. *Simple Ionic Salts.* Simple ionic salts (without complex ions) are not piezoelectric, while simple homopolar salts are often active. For example, no anhydrous halides of the alkali or alkaline earth metals have been shown to be piezoelectric. This is no longer true as the character of the bond becomes more homopolar so that many compounds of the AX type are piezoelectric, for example, CuCl and ZnS.

2. *Salts Containing Radicals that Lack a Center of Symmetry.* These salts are often piezoelectric. Thus, there are several chlorates, bromates, iodates, and dihydrogen phosphates that show activity. In most of these salts the structure can be pictured as containing a discrete anionic group or radical.

The sulfate, perchlorate, and phosphate radicals are tetrahedral in shape and as such lack a center of symmetry. Yet many anhydrous sulfates, perchlorates and phosphates are inactive, indicating that this asymmetry in the radical is not always reflected in the lattice. For example, K_2SO_4 is not piezoelectric.[4] However, if we substitute one Li^+ for one of the K^+ ions in K_2SO_4 we obtain an active crystal, $LiKSO_4$. The change in ion environment of the SO_4^{--} as a result of this substitution has emphasized the asymmetry of the SO_4 radical through polarization and rendered the crystal piezoelectric.

An attempt will be made to show that, given a radical lacking a center of symmetry and the proper ion environment, the crystal will be found to be piezoelectric. For activity in the lattice the lack of a center of symmetry in the radical is not a sufficient specification.

Salts Containing Radicals of Octahedral, Planar or Tetrahedral Form. These are usually not piezoelectric. Typical octahedral ions whose simple salts are not piezoelectric include SiF_6^{--}, $SnCl_6^{--}$, and $PtCl_6^{--}$. The same applies to planar complexes such as $PtCl_4^{--}$. This generalization is not however, intended to apply to compounds with two complex radicals. For example, $Be \cdot 4H_2O$ forms a tetrahedral complex in $BeSO_4 \cdot 4H_2O$[5] which shows moderate piezoelectric activity.

The essentially planar NO_3^{--} and CO_3^{--} also usually result in inactive compounds, but are more easily distorted as in the case of Rb and

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[4] It has been suggested that the inactivity of these tetrahedrally shaped-XO_4 salts might be explained on the basis that adjacent tetrahedra would be so placed as to possess, together, a center of symmetry. Examination of typical XO_4 structures does not show any such arrangements of the units in these salts.

[5] Wells, A. F., Structural Inorganic Chemistry, Oxford University Press (1945), pp. 369.

Cs salts. Several complex nitrates such as $Ce(NH_4)_2(NO_3)_5 \cdot 4H_2O$ and $KLa(NO_3)_4 \cdot 1\frac{1}{2}H_2O$ are active and do not lend themselves to this generalization, again because of the presence of H_2O and the multiple cations. None of the simple carbonates are active although several mixed carbonates such as $LiNaCO_3$ do exhibit piezoelectricity.

The following tabulation shows (by a +) which of the chlorates, bromates, and iodates combined with univalent cations are active:

	Li	Na	K	Rb	Cs	Ag	H
ClO_3		+				+ (high form)	
BrO_3		+	+	+	+		
IO_3	+		+	+?	+?	+	+

The chlorate and bromate structures are similar,[6] the X atom of the XO_3 group being located at the apex of a low pyramid with the unshared pair of electrons occupying the 4th tetrahedral position. Here the radical XO_3 exists as a discrete building unit since the coordination of X for O is according to the chemical formula. The building unit, like all tetrahedral-shaped ions, is without a center of symmetry.

Of the chlorates only three active crystals are known: sodium, silver (high form) and strontium. No simple reason can be given for the inactivity of the other members except to say that of these anions, the polarizability of the ClO_3^- would be the least.

If an increase is made in the size of the central X ion in the XO_3 structure, as in BrO_3^-, an increase in the number of active salts is found. This would seem to indicate that the increased polarizability of the bromate ion by the cation has further emphasized the asymmetry of the radical.

Iodic acid, which consists of hydrogen-bonded, discrete IO_3 groups, is strongly piezoelectric. It is believed that the hydrogen bonding is responsible for the activity, possibly because it further emphasizes the asymmetry of the units from which the lattice is built.

With the exception of sodium iodate, all the alkali iodates are active, as is silver iodate. However, the iodine has a much higher coordination for the oxygen ion than has chlorine or bromine, so that a three-dimensional network results. Therefore, we can no longer speak of discrete anions or radicals. In the series Li-Na-K-Rb-Cs the cation coordination for O^{--} is respectively 6-10-12-12-12. The inactive $NaIO_3$, has a deformed perovskite structure, while the active potassium, rubidium, and cesium iodates have a normal one. Even in the absence of discrete building blocks, the possibility of the polarization of the large I ion lends itself to the picture of an anionic asymmetry within the lattice.[7]

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[6] Wells, *Op. Cit.*, pp. 272–273.

[7] Among the other XO_3 salts we can list one other piezoelectric material, $BaTiO_3$. This crystal has a structure similar to KIO_3.

The Phosphates. Of the univalent and bivalent tertiary phosphates only Ag_3PO_4 is active, despite the fact that all of these phosphates contain a tetrahedrally shaped anion which lacks a center of symmetry. It is of interest to note that in the case of Ag_3PO_4 the P-O distance is increased, although it is normally constant in other orthophosphates. The strong polarization of the PO_4 group by the Ag ions has enhanced the asymmetry of this group to produce the directional properties necessary for piezoelectricity. Ag_3AsO_4 has a similar behavior and structure. This polarization of the silver arsenate and phosphate is also evident in their respective colors, chocolate brown and yellow. In the case of aluminum orthophosphate $AlPO_4$ which is piezoelectric and isotypic with quartz ($SiSiO_4$), it is probably not correct to speak of anionic groups, as the isotypic quartz lattice is a three-dimensional network. The O ions are certainly strongly polarized, however, by the trivalent Al and the pentavalent P.

The tabulation below indicates the piezoelectric activity of the $H_2PO_4^-$ salts. In these salts, as far as is known, complete substitutions of D^+ for H^+ and of As^{5+} for P^{5+} are possible:

	$H_2PO_4^-$	$H_2AsO_4^-$
Na	+ (H_2O)	+ (H_2O)
K	+	+
Rb	+ (Tetr. form)	
Cs	—*	
NH_4	+	+

+ Indicates activity.

— Indicates inactive salt.

* Not isomorphous.

The following cation substitutions have been reported:[8, 9]

SOLID SOLUTION IN XH_2PO_4

	Substituting Ions				
X	K	Rb	Cs	NH_4	Tl
KH_2PO_4	—	L	L	C	L
KH_2AsO_4	—			C	
$NH_4H_2PO_4$	C	L	L	—	L
$NH_4H_2AsO_4$	C			—	

L Indicates limited solid solution.

C Indicates complete solid solution.

(Incomplete data indicate that the same solid solution relations apply to the arsenate substituted compound.)

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[8] The following selected references are of interest: Bartschi, P. et al., *Helvetica Physica Acta*, **18**, 240 (7/16/47); Matthias, B., and Merz, W., *Idem* **19**, 227 (7/31/46).

[9] Report No. 1 *NDRC Project* 17.3–11 (2/1/43)—unpublished data of Mueller, H. *et. al.*

In these salts the building unit is a hydrogen-bonded PO_4 group. In fact, the O-H-O distance in KH_2PO_4 is the smallest such distance known.[10]

The otherwise inactive PO_4 group is rendered active by the bonding to the cations through hydrogen and the resulting asymmetry of the building unit. The monohydrates $NaH_2PO_4 \cdot H_2O$ and $NaH_2AsO_4 \cdot H_2O$, are moderately active and fit into the above picture.

However, the inactivity of one of the forms of RbH_2PO_4 and of CsH_2PO_4 is not so readily explained except perhaps on the basis of an extreme distortion of the H_2PO_4 group.

The Anhydrous Sulfates. As mentioned earlier the anhydrous sulfates are usually inactive. The exceptions to this statement are the anhydrous sulfates which contain a large and a small cation. For example, some of the $MLiSO_4$ salts are active, where M^+ can be the univalent ions Na^+, K^+, and NH_4^+. The mutual presence of a small and a large cation acts on the SO_4 group to produce a one-sided polarization in the structure, as it does in the mixed carbonates. Selenium can be substituted completely, and Cr^{6+} and Mo^{6+} partially, in these sulfates without loss of activity.[2]

Hydrated Sulfates and Related Compounds. The dithionates of potassium, rubidium, cesium, barium, strontium, and lead are piezoelectric. The dithionate ion consists of two SO_3 groups linked through the sulfur atoms, and has a center of symmetry.[11] Thus the dithionate complex offers an exception to the relation of mutual asymmetry in radical and lattice.

The list of active hydrated compounds can be summarized as follows:

$Li_2SO_4 \cdot H_2O$
$BeSO_4 \cdot 4H_2O$
$NiSO_4 \cdot 6H_2O$
$LiClO_4 \cdot 3H_2O$

$$\left.\begin{array}{ll} \text{Series:} & \left.\begin{array}{l} MgSO_4 \cdot 7H_2O \\ ZnSO_4 \cdot 7H_2O \\ NiSO_4 \cdot 7H_2O \end{array}\right\} \\ \\ \text{Series:} & \left.\begin{array}{l} MgSO_3 \cdot 6H_2O \\ NiSO_3 \cdot 6H_2O \\ CoSO_3 \cdot 6H_2O \end{array}\right\} \end{array}\right> \text{and their respective solid solutions}$$

The salt $NiSO_4 \cdot 6H_2O$ has a group $Ni(H_2O)_6^{++}$ but the coordination arrangements for the six water molecules are not identical and the group, therefore, cannot be considered as similar to the octahedrally shaped $Fe(CN)_6$ radical.[12] A similar situation probably holds for the hexahydrated sulfites.

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[10] Pauling, L., Nature of the Chemical Bond, Cornell University Press (**1945**), pp. 311.
[11] Wells, *Op. Cit.*, pp. 305.
[12] Wells, *Op. Cit.*, pp. 368–369.

In the case of the heptahydrate series, there are octahedral groups $M(H_2O)_6$ with the seventh water molecule held between these groups and the anions.

The structure of $BeSO_4 \cdot 4H_2O$ is a packing of SO_4 tetrahedra and $Be(H_2O)_4$ groups.[5] Here the water molecules have an identical arrangement, but are under strong polarizing influence of the small Be ion. The monohydrate of lithium sulfate is an unusually strong piezoelectric material. In this salt the coordination of the two lithium ions is different; one has an environment of a water molecule and three O ions, while the other is surrounded by four O ions. The lithium perchlorate $LiClO_4 \cdot 3H_2O$ belongs to an isomorphous family of salts which have much the same structure as the sulfate hexahydrates, the lithium being surrounded octahedrally by six water molecules.[13] Again the presence of a small ion must act to produce those conditions in the lattice that make it piezoelectric.

In the case of the numerous alums $MAl(SO_4)_2 \cdot 12H_2O$ and schönites or picromerites $M_2^{I}M^{II}(SO_4)_2 \cdot 6H_2O$ the coordination of the various cations by the water molecules is perfectly symmetrical, thus giving no cause for asymmetry in the lattice. None of these salts is active.[14]

It should be mentioned that Se^{6+} can replace S^{6+} in any of the above sulfates, either in whole or in part, without loss of piezoelectric activity.[2]

SUMMARY

This investigation of piezoelectric activity in available inorganic crystals has attempted to find a relationship between crystal structure and the presence of activity.

It will be recalled that all of the active compounds studied belong to crystal classes which lack a center of symmetry. Many of them also contain a complex ion which likewise lacks a center of symmetry. It should be pointed out, however, that not all salts containing such asymmetric radicals are active.

The study has indicated that two conditions are, in general, characteristic of piezoelectric structures: (1) they contain an asymmetric radical, and (2) the ion environment of this radical is such that it further emphasizes the asymmetry.

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[13] Wells, *Op. Cit.*, pp. 370.

[14] Wells, *Op. Cit.*, pp. 180.

SOME OBSERVATIONS ON THE CRYSTALLIZATION OF SILICIC ACID

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Abstract

In the presence of calcium, added as $CaCO_3$ or $CaSiO_3$, the crystallization of amorphous silicic acid by heating at 1150° C. produces a mixture of quartz and cristobalite. Heating of the pure silicic acid at this temperature results in cristobalite only. The generation of quartz some 300° C. above the quartz-tridymite transition temperature, in the presence of calcium, is noteworthy. Investigation of the effects of other additives and of other firing temperatures is being carried out.

In a recent paper on the preparation of luminescent wollastonite (1) by the reaction of calcium carbonate and amorphous silicic acid, it was reported that quartz was found in the product when an excess of $SiO_2 \cdot xH_2O$ was used. This observation was surprising for two reasons: first, because it was at variance with statements in the literature that the crystallization of amorphous silica results only in cristobalite (2, 3); and second, because the firing temperatures employed in the above-mentioned work were some 300° C. above the quartz-tridymite transition temperature (4). It was, therefore, considered of interest to repeat these experiments, particularly since the preparation of the luminescent $CaSiO_3$ was complicated by the necessity of adding manganous carbonate and lead fluoride as "activators" for the luminescence.

The silicic acid employed in these experiments was Mallinckrodt "Special Bulky" silicic acid commonly used for the preparation of luminescent silicates. It appears that this silicic acid is made by precipitation of a sodium silicate solution with acid, followed by intensive washing to remove the soluble salts. Spectrographic analysis showed that the material contained 0.003% Na and 0.008% K by weight. The only other impurities detected were Mg, Fe, and Al, all of which were of the order of 0.002–0.003% by weight, and about one part per million of Cu. The water content of the silicic acid is variable, and averages about 10–15%. This finely-divided, high-purity silicic acid is made on a large scale for use in the synthesis of commercial fluorescent lamp and cathode ray tube phosphors and is readily available. The other reagents used in the present work were Baker's C. P. calcium carbonate and Baker's C. P. zinc oxide.

$CaCO_3$–$SiO_2 \cdot xH_2O$ mixtures in the proportions 1:1, 1:2, 1:5, 1:7.5, 1:10, 1:50, and 1:100 were made by milling the components with distilled water for two hours in pint porcelain ball mills equipped with flint pebbles. The mixtures were then filtered, dried for two to three hours at 110° C., and fired in Vitreosil or Amersil fused silica trays at 1150° C.

TABLE 1

Phases present in $CaCO_3-SiO_2\cdot xH_2O$ mixtures heated three hours at 1150° C.

CaO/SiO_2 Ratio	Phases Identified from Powder Photograph
1:1	Wollastonite predominant; possibly quartz (one weak line, $d=4.3$)
1:2	Wollastonite; quartz; cristobalite
1:5	Quartz predominant; some wollastonite; cristobalite
1:7.5	Quartz predominant; some wollastonite; cristobalite
1:10	Quartz predominant; trace of wollastonite; cristobalite
1:50	Quartz predominant; trace of wollastonite; cristobalite (one line, $d=4.04$) (poor pattern)
1:100	Amorphous pattern

for three hours. The samples were loaded into a furnace which was already at temperature, the furnace recovering its 1150° C. temperature within 15 minutes after the samples were placed inside. At the conclusion of the firing the samples were removed from the hot furnace, and reached room temperature in about 15 minutes.

Powder patterns of the various samples were taken with filtered CuK radiation, and compared with patterns of natural quartz (source unknown), cristobalite from Cerro Montosa, New Mexico, and wollastonite from Inyo County, California, as well as with data from the *A.S.T.M.* tables. The results are given in Table 1 and Fig. 1.

The 1:100 CaO/SiO_2 sample was replaced in the furnace at 1150° C. and refired for $3\frac{1}{2}$days. A powder photograph (cf. Fig. 1) then gave a very good quartz pattern. The presence of cristobalite was also established in this sample from the single line, $d=4.04$ Å. Microscopic examination by O. F. Tuttle of the Geophysical Laboratory confirmed the presence of both the quartz and the cristobalite in this sample. The microscopic examination showed that cristobalite was the major component of the mixture, and that it was of very low particle size; the quartz, although present in smaller amounts, occurred as considerably larger crystals. The predominance of quartz lines in the diffraction pattern is apparently due to this situation.

A fired sample of the 1:1 CaO/SiO_2 composition was mixed with four more moles of amorphous $SiO_2\cdot xH_2O$, and refired overnight at 1150° C. The powder photograph of this preparation showed the quartz pattern predominant, and was indistinguishable from the diffraction pattern given by the 1:5 CaO/SiO_2 sample made directly from $CaCO_3$ and silicic acid.

In order to insure that the fused silica firing vessels were not affecting

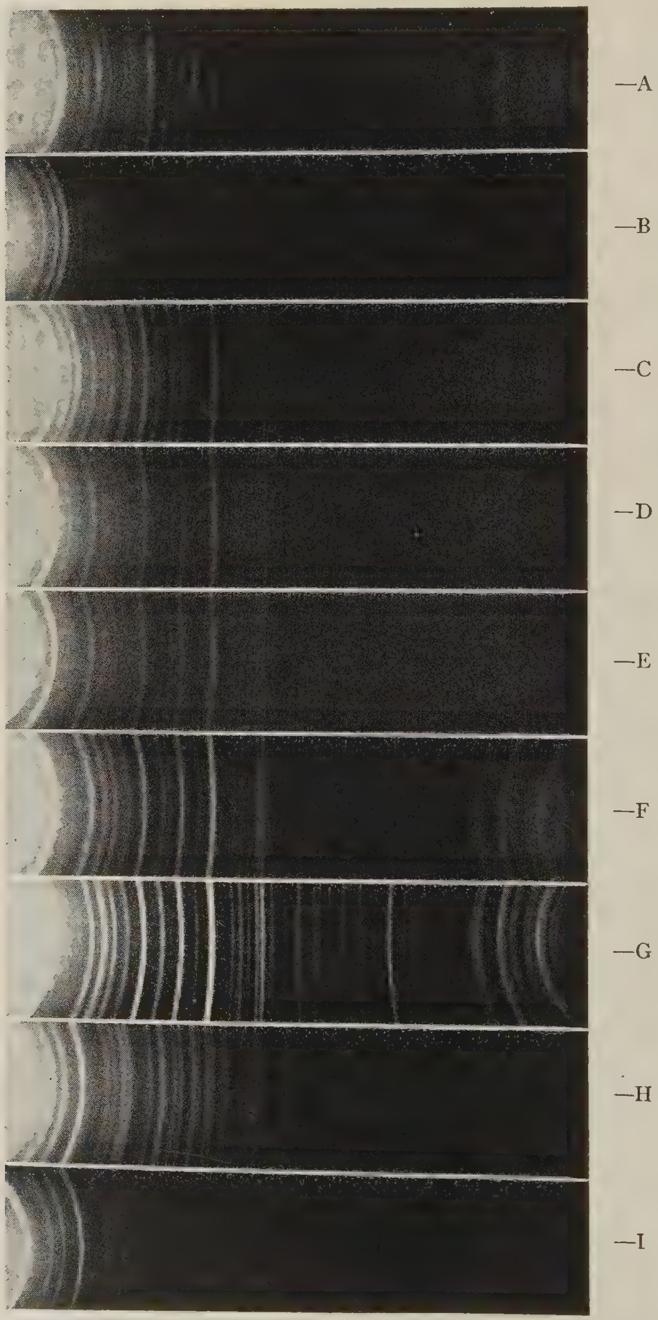

FIG. 1. X-RAY POWDER DIFFRACTION PATTERNS Cu K-radiation, Ni filter.

the results, mixtures with 1:5 and 1:50 $CaCO_3/SiO_2 \cdot xH_2O$ were made up by pebble milling as above and fired in platinum crucibles for three hours at 1150° C. The diffraction patterns were identical with those obtained when the firings were made in silica trays.

The original silicic acid was amorphous to x-rays, and remained so after successive firings of three and sixteen hours. After 4½ days of uninterrupted firing at 1150° C. a powder photograph of the product checked that of cristobalite line for line.

It was thought that perhaps the abrasion of the flint pebbles during the milling of the calcium carbonate-silicic acid mixtures might have had some effect on the subsequent crystallization of the latter, hence the following experiments were performed to check this point. Two samples of silicic acid were milled in the usual way, the first with distilled water and the second with redistilled acetone as the liquid medium. After filtration and drying, these samples were fired at 1150° C. along with a sample of unmilled silicic acid. The charges were removed from the furnace daily in order to take samples for powder photographs, and then replaced. Amorphous patterns were obtained from all three samples for the first ten days. After eleven days the unmilled silicic acid gave a good cristobalite pattern, while the two milled samples remained amorphous. After thirteen days a good cristobalite pattern was obtained from the acetone-milled silicic acid, and a very poor cristobalite pattern was obtained from the water-milled material. It was somewhat unexpected, although not unreasonable, that the interruption of the firing for about an hour every day should slow down the crystallization rate of the unmilled silicic acid by a factor of two or three. The further slowing down of the crystallization rate due to the water milling may be due to the removal of some of the residual alkali from the silicic acid by this treatment, acetone being presumably much less effective in this regard. In any event, these experiments showed that the generation of quartz is not ascribable to the effect of impurities ground off the flint pebbles or the porcelain mill during the mixing procedure.

A—natural wollastonite
B—1:1 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
C—1:2 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
D—1:5 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
E—1:10 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
F—1:100$CaCO_3$—SiO_2, heated 3½ days, 1150° C.
G—Natural quartz
H—H_2SiO_3, heated 4½ days, 1150° C.
I—natural cristobalite

As a final check on this point, slurries of $CaCO_3$ and $SiO_2 \cdot xH_2O$ in the mole ratios of 1:5 and 1:50 were made up by adding distilled water to the powders in bakelite-capped glass bottles and gently agitating the suspensions for two hours. In this case no grinding pebbles were used. The slurries were filtered, dried, and fired in platinum crucibles at 1150° C. for three hours. The 1:5 CaO/SiO_2 sample gave a powder photograph which checked earlier preparations of this composition, while the 1:50 CaO/SiO_2 sample gave a practically amorphous pattern. After the samples were reheated at 1150° C. for about 55 hours, the 1:5 CaO/SiO_2 preparation showed no change in its pattern, while the 1:50 CaO/SiO_2 sample gave a powder pattern similar to that of the 1:5 CaO/SiO_2 preparation. The failure of the 1:50 CaO/SiO_2 mixture to crystallize in three hours in this experiment seems readily understandable in view of the poorer dispersion of the $CaCO_3$ by the less vigorous mixing technique employed here.

The possibility is not excluded that the initial formation of quartz nuclei may occur below the quartz-tridymite transition temperature even in the short time involved in heating up the $CaCO_3$–$SiO_2 \cdot xH_2O$ mixture. We have attempted to minimize this heating-up time by using small charges and furnaces of large heat capacity. In the experiments with the $CaCO_3$–$SiO_2 \cdot xH_2O$ slurries, for example, 30 ml. platinum crucibles were used as firing vessels. When two of these were placed in a furnace with a hot chamber 7″×10″×18″, the thermocouple temperature dropped to 1110° C. during the loading, and recovered its 1150° C. temperature within three minutes. We are, therefore, inclined to discount this possibility as an explanation of our results.

If this explanation is ruled out, and if the data of Fenner (4) placing the quartz-tridymite transition temperature at $870 \pm 10°$ C. are correct, it would appear that we have here a case of the generation and persistence of a low temperature polymorphic form above its stability region. The anomalous generation and continued existence of high temperature polymorphic forms below their stability range is a very common phenomenon in mineralogy and chemistry. The inverse situation—although a priori equally possible—seems to have been seldom observed, the only other example known to us being the generation of arsenolite, the low temperature form of As_2O_3 (arsenolite-claudetite transition temperature $= -13°$ C.) (5) which readily precipitates from solutions of arsenious oxide at room temperature, and even at a few hundred degrees above room temperature from the vapor.

Experiments with the addition of ZnO, analogous to those performed with the calcium carbonate additions, were carried out, mixing of the components being carried out entirely by pebble milling, and the firings being conducted in fused silica trays at 1150° C. Willemite and cristobalite were the only phases found in these runs.

It is planned to continue these studies using different sources of amorphous silica, with other additives, and at other temperatures.

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X-RAY SPECTROMETER STUDY OF MICA POWDERS

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ABSTRACT

The diffraction patterns of mica powders were used to test the reproducibility of various methods of powder sample preparation with a recording Geiger-counter-*x*-ray spectrometer. The method described proved satisfactory and is suitable for the preparation of all types of powders. The diffraction patterns of twelve micas are given and it is noted that differences occur for similar varieties obtained from different localities.

INTRODUCTION

A suitable method for the preparation of powder samples is particularly important in studies where a large flat sample area is required as with the Norelco *x*-ray spectrometer. In many cases, this instrument is being used to study materials having relatively weak patterns (e.g. clay minerals) so that wider slits than usual must be employed. With wider slits, however, the image of the beam upon the sample is considerably larger. Furthermore, the clay minerals have reflections at very low glancing angle (e.g. 5°) where the irradiated area is several times greater than at 30°. Thus, a large powder sample area must be obtained.

Powder samples of the pure micas are especially difficult to prepare since the cleavage planes are so very well defined. Thus an investigation of the *x*-ray diffraction patterns of this group of minerals was undertaken primarily to test for the most satisfactory method of powder sample preparation.

Since random orientation is so hard to achieve with the micas, it is also difficult to compare the results of different investigators using different methods of sample preparation. The present study includes the diffraction patterns of 12 micas: eastonite, 2 lepidolites, 2 muscovites, 3 biotites, 3 phlogopites and 1 zinnwaldite. Identical conditions were used to obtain the patterns so that the observed intensities may be directly compared.

SAMPLE PREPARATION AND PROCEDURE

When a large sample area must be obtained, it is important and sometime difficult to pack the powder so that it remains firm throughout the investigation. This is determined by the packing quality of the powder, the particle size and also by the shape of the aperture in the holder and the degree of packing of the powder. The preparation time of the sample often depends very largely on the grinding time of the material investigated. The preparation of a relatively large quantity of fine powder from

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hard minerals e.g. bytownite or substances such as the micas requires a tremendous amount of time and effort if the grinding is done by hand. There are, however, several commercial automatic mortar grinders which are very timesaving and convenient. The machines having tungsten or boron carbide grinding surfaces are particularly worthwhile.

Two sample holders were finally used to obtain reproducible patterns. One holder with a rectangular opening $\frac{3}{8}\times 2\frac{1}{4}$ inches ($.9\times 5.7$ cm.) and a smaller one with a circular opening 9/16 inch (1.4 cm.) in diameter. It was found early in the work that any pressure across the surface of the prepared sample resulted in orientation. The method finally adopted was that proposed by G. L. McCreery (1) of the Ohio Brass Company.

The mica is ground to pass 325 mesh and deposited through a small funnel, containing a 60 mesh screen, upon a glass plate backed on the holder with scotch tape. When the holder is filled to heaping it is packed gently in vertical strokes with a spatula and a second glass plate placed over this surface. The unit is then turned over and the original plate removed exposing the prepared sample surface. The second glass plate is then secured with tape. Great care must be exercised to avoid sliding the first plate when it is removed since this is sufficient to orient the particles.

The method of sample preparation was tested through the reproducibility of the mica patterns from one packing to another. It is significant that the smaller holder gives the more reproducible mica patterns probably because the powder is more easily packed and remains more firm. The intensities may vary by a few per cent from one packing to the next but not significantly. This is not true, however, of the large holder. The intensities of the two strongest lines from the (001) cleavage plane may vary by 20 to 30 percent from a previous set of intensities. In a few cases, however, an additional weak reflection appears when the large holder is used. This seems to indicate that although the pattern obtained with the small holder is reproducible, the orientation of the particles is still not completely random. The smaller holder is probably more satisfactory when semi-quantitative and quantitative results are desired. However, in order to obtain a complete pattern for a given material it may be necessary to refer to the greater surface of the rectangular type holder for possible supplementary reflections.

Discussion of Results

Five runs were made of each sample and for each reflection the mean values of the interplanar spacings, *d*, and the intensities tabulated.

The slits were set at 4 mm. high and 2.3 mm. and 1 mm. wide at the *x*-ray and counter slits, respectively. These settings were used when both tubes had Lindemann glass windows and correspond to the widest slit settings. When mica windows were used in both tubes, the intensity increased by a factor of 3 and similar values were obtained using the narrow x-ray slit and medium wide counter slit. These correspond to approximately .8 mm. and .5 mm. wide. The chart speed was set at $\frac{1}{2}$ inch per minute with a scanning motor speed of 1 r.p.m. Since the patterns are generally diffuse, there was no advantage in reducing the speeds.

For comparison of intensities, a sample of quartz powder was run under the same conditions so that intensities might be directly compared. The values for quartz are given in Table 1. The interplanar spacings in Angstrom units (*d* values) and the recorded intensities are given in Tables 2 to 7.

TABLE 1. SPECTROMETER PATTERN OF QUARTZ STANDARD

d	*I*	Index *I*	*d*	*I*	Index *I*
4.25	63	(25)	1.661	9	
3.35	230*	(100)	1.544	40	
2.45	32		1.454	6	
2.29	24		1.289	6	
2.24	15		1.259	9	
2.13	24		1.230	6	
1.983	16		1.202	12	
1.822	50	(25)			

* By extrapolation from weaker pattern.

On the whole, the lines are fairly wide and the angular values of the reflections should be accurate within 0.1° in 2θ. Lines marked "w" are wide or diffuse and lines marked "vw" are very wide and in general the assigned value of 2θ is merely the center of a band or hump. All intensities are measured above the local background and the intensity of the background proper is listed at the end of every table for the 2θ values 70° and 8°. The latter values may serve as an indication of the relative fluorescence of the different samples.

The diffraction patterns of the micas have been obtained by Magdefrau and Hofmann (2), Nagelschmidt (3), Jackson and West (4), Hendricks (5), and others. Since their data were obtained with small powder cameras or single crystals, the spectrometer values are given here for comparison. It is evident from the A.S.T.M. index and from the present data that there are differences in the diffraction patterns of the same variety of mica obtained from different localities. The differences may be in the relative intensities of the reflections or in the *d* values.

In general, the reflections from the first and third orders of the cleavage plane (001) are considerably stronger than the others and the reproducibility of their intensities is a very sensitive test for orientation in the sample. Eastonite, given in Table 2, appears to be the only exception in the group since these reflections are distinctly of secondary importance.

TABLE 2. SPECTROMETER PATTERN FOR EASTONITE, EASTON, PENNSYLVANIA

d	*I*	*d*	*I*
10.10	23	1.800	6 w
7.30	100	1.688	3 vw
5.06	3 w	1.538	6 w
4.61	4 w	1.508	9
3.66	79	1.463	3 vw
3.39	20	1.435	3 vw
3.17	4 w	1.375	3 vw
2.94	3 vw	1.282	5 vw
2.74	2 vw	1.222	2 vw
2.63	3 vw		
2.51	11 w	Background	
2.44	10		
2.16	7 w	14.72	17
2.03	7 w	1.342	4
1.830	6 w		

TABLE 3. SPECTROMETER PATTERNS OF LEPIDOLITE

d	Ohio City, Colorado	Hebron, Maine	*d*	Ohio City, Colorado	Hebron, Maine
10.10	21	8	2.00	10	10
5.01	12	6	1.702	3 vw	3 vw
4.48	10 w	10	1.639	2 vw	2 vw
3.88	3 vw	4 vw	1.588	2 vw	2 vw
3.65	10	8	1.544	4	
3.50	5	9	1.508	8 w	8 w
3.35	22	10	1.492	2 w	2
3.21	7	9	1.433	5	4
3.09	13	9 w	1.304	5 vw	5
2.99	2		1.224	6 w	4
2.90	8 w	8 w			
2.86	3	2	Background		
2.80	4 w	4 w			
2.67	2 w		14.72	28	29
2.58	21	24	1.342	8	6
2.49	4 vw	3			
2.43	5 vw	8 vw	cf. Index Cards: II—994		
2.26	4 vw	2 vw	II— 63		
2.03	10	10			

The patterns of the lepidolites given in Table 3 are similar although the two strong lines are both stronger in the sample from Ohio City, Colorado.

A comparison of the two muscovites in Table 4 shows that the sample from Irwin, Tennessee, has a far richer pattern than that from Chester, Pennsylvania. The intensities of the two strong lines are greater in the former and their ratios are reversed.

Table 4. Observed Patterns of Muscovite

d	Chester, Pennsylvania	Irwin, Tennessee
10.00	8	60
5.01	4	14
4.50	8 w	16
4.31		5
3.90	5 w	8
3.75	4 w	8
3.52	5 w	10
3.35	15	48
3.22	5 w	14
3.00	7	14
2.88	4 w	9
2.80	4 w	15
2.58	15	21
2.51		8 w
2.47		5
2.40	5 w	8
2.15	5 vw	6
2.14		9 w
2.06	2	2
2.03	10	10
2.00	7	3
1.979	3 w	
1.664		7 vw
1.653	6 vw	10 vw
1.610	3 vw	3 vw
1.563		3 vw
1.546		3 vw
1.528	2 vw	5 vw
1.510	6 w	9 w
1.459	2 vw	2 vw
1.433	3 vw	5 w
1.391		2 vw
1.368		3 vw
1.354	4 vw	6 vw
1.342		3 vw
1.322		2 vw
1.298		5 vw
1.279		3 vw
1.265		3 vw
1.224		7

Background

d	Chester, Pennsylvania	Irwin, Tennessee
14.72	33	34
1.342	14	13

cf. Index Cards: II—2177
II—2109
II—1026
II— 71
II— 67

The relative intensities of the lines from the cleavage plane are similar in the three biotites given in Table 5. It is evident, however, that small differences occur between the samples from Franklin, New Jersey, and Tromo, Norway. The biotite from Nahant, Massachusetts, is strikingly different with a very high background and only the strongest lines appearing. This sample was also run using an Fe target but the background remained high and little change was found.

TABLE 5. SPECTROMETER PATTERNS OF BIOTITE

d	Franklin, N. J.	Tromo, Norway	Nahant, Mass.
10.04	45		25
9.93		36	
4.64	4 vw		
4.57		4 vw	
4.28		5 vw	
3.65	4 w	4 vw	
3.54	3 w		
3.37	34		17
3.35		22	
3.29	3 w		
3.14		5 vw	
3.07			3 vw
3.04	6 w		
2.93	3 vw	3 vw	
2.83	5		
2.63	18		8 w
2.61		19	
2.53	5	5 vw	2 w
2.45	10		5 w
2.43		9 w	
2.28	4 w		
2.19	9 w		2 vw
2.17		7	
2.03	5	5	6
1.991		5	
1.912	2 vw		
1.744	3 vw		
1.682	10	7	3 vw
1.634	3 vw		
1.608	3 vw		
1.550			5 vw
1.544	13 w		
1.537		11 w	
1.528	4 w		
1.517		3 w	
1.433	8	5 w	5
1.368	4 w	5 w	
1.332	2 w		
1.221	8	7 w	8
	Background		
14.72	40	40	59
1.342	18	17	39

cf. Index Cards: II—2010
II— 70
II— 56

TABLE 6. SPECTROMETER PATTERNS OF PHLOGOPITE

d	Clark Hill, N. Y.	Vromans Lake, N. Y.	Burgess, Ontario
10.04	26	19	33
5.05		3.5 vw	
5.01	4 w		
4.62		5 vw	7 vw
4.60	6 vw		
4.31	6		
4.27			2 vw
4.04	2 vw		
3.95	3 vw	3 vw	5 vw
3.69		4 vw	
3.68			10
3.66	5 w		
3.36	45	30.5	21 (w)
3.15	11	8.5	7
3.05	6	5	3 w
2.94			7 w
2.93		6	
2.92	8		
2.80		3 w	
2.79	2 w		
2.73			5 w
2.72	5	3	
2.63	16	22	20
2.53	8	7	5 w
2.46	9		
2.45		6	
2.44	10	10	8 w
2.30	6	3 vw	2 vw
2.27	3	9 w	
2.18			7 vw
2.17	8	11	
2.13	5		
2.10	3	4	
2.04			7
2.03	8	6	
2.01			5 vw
2.00	12	10	
1.983	5		
1.908	2 vw	2 vw	
1.878	2 vw		
1.829	6	2 vw	
1.744		7	
1.702	2 vw		2
1.679			7 w
1.673	12	12 w	
1.651	2 vw		3 vw

TABLE 6. (*Cont.*)

d	Clark Hill, N. Y.	Vromans Lake, N. Y.	Burgess, Ontario
1.621	2 vw	3 vw	
1.573		2 vw	2 vw
1.537	14 w	16	13
1.523			4 vw
1.519	3 w	5 vw	
1.503		2 vw	1 vw
1.479		2 vw	2 vw
1.435	5 w	3 vw	3 vw
1.398		2 vw	
1.377	6 vw		
1.368			3 vw
1.363	5 vw	5 vw	
1.328	3 vw	3 vw	4 vw
1.310	3 vw	2 vw	3 vw
1.259	3 vw		
1.224	4	7 w	4 w
	Background		
14.72	30	22	26
1.342	6	8	5
	cf. Index Card: II—65		

The patterns of the phlogopites given in Table 6 are the richest of the group and the tendency of the powder to become oriented was most pronounced.

TABLE 7. SPECTROMETER PATTERN OF ZINNWALDITE, WINTERHAM, VIRGINIA

d	*I*	*d*	*I*
10.04	20	2.29	3 vw
4.57	6 w	2.17	6 vw
4.19	3 vw	2.04	4 vw
3.88	3 w	1.991	6
3.68	6 vw	1.682	5
3.34	17	1.667	6 vw
3.25	3	1.526	6 vw
3.12	9		
3.05	3	Background	
2.93	6 w		
2.70	3	14.72	35
2.62	18	1.342	25
2.56	3		
2.49	4	cf. Index Card: II—66	
2.43	5 w		

Zinnwaldite in Table 7 has a high background although not as great as the Nahant biotite.

TABLE 8. PATTERN OF CLEAVED MICA SURFACE

d	Order	*d*	Order
10.0	1	2.0	5
5.0	2	1.67	6
3.33	3	1.43	7
2.5	4		

CONCLUSIONS

Reproducible diffraction patterns can be obtained for powder samples by the method outlined earlier. In the vast majority of cases it should be possible to achieve completely random orientation of the particles. In the case of the most difficult type of sample to prepare, namely the micas, it is still possible to achieve reproducibility and to approximate random orientation.

The diffraction patterns of the micas studied show that the d values and intensities of the reflections differ from one variety of mica to another and within the same variety.

The intensities of the reflections at $d = 10.0$ and 3.3 are strongly affected by slight orientation in the sample. It might be useful to describe the patterns of mica by means of a secondary set of intensities where the reflections of the cleavage plane are omitted. This should remove considerable distortion in the intensity ratios when the orientation, though slight, is sufficient to influence the strongest reflections.

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THE CORREGO FRIO PEGMATITE, MINAS GERAIS:
SCORZALITE AND SOUZALITE, TWO NEW PHOSPHATE MINERALS[1]

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ABSTRACT

This paper describes the structure and mineralogy of a pegmatite that has yielded three new phosphate minerals in recent years. The pegmatite is well zoned into three structural units of characteristic texture and mineral association. The minerals present include albite, muscovite, quartz, scorzalite (new mineral), souzalite (new mineral), brazilianite, apatite, zircon, tapiolite, and two unidentified phosphate minerals. Detailed descriptions, with chemical analyses, are given for scorzalite and souzalite, both of which are hydrous iron magnesium aluminum phosphates. Scorzalite is isomorphous with lazulite; the structural relationships of souzalite are not known.

INTRODUCTION AND ACKNOWLEDGMENTS

This paper contains a detailed description of the structure and mineralogy of the Corrego Frio pegmatite, Minas Gerais, Brazil, which has yielded three new phosphate minerals since its discovery in 1942. Two of these new minerals, scorzalite and souzalite, are described in this paper. Additional information on brazilianite, described in 1945, is also presented.

The authors are indebted to a number of colleagues in the Section of Geochemistry and Petrology, U. S. Geological Survey, for courteous assistance in mineral study. K. J. Murata made spectrographic analyses of scorzalite and souzalite that served as a guide for the chemical analyses by Fahey. J. M. Axelrod took *x*-ray powder diffraction photographs of the new phosphate minerals and prepared the mount reproduced in figure 3. E. S. Larsen 3d was helpful in the precise determination of the optical constants of scorzalite and souzalite. Theodore Botinelly made microchemical tests for phosphorus and other elements in two unidentified minerals in the collection. Marie L. Lindberg assisted in purifying two samples for analysis. E. S. Larsen 3d, Michael Fleischer, and Earl Ingerson, all of the Geological Survey, critically reviewed this paper and made several suggestions for its improvement.

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[1] Published by permission of the Director, U. S. Geological Survey. Paper read before the Mineralogical Society of America, Ottawa, Canada, December 30, 1947.

Location

The Corrego Frio pegmatite is in eastern Minas Gerais, Brazil (see Fig. 1) near the village of Divino and approximately 40 km. north of

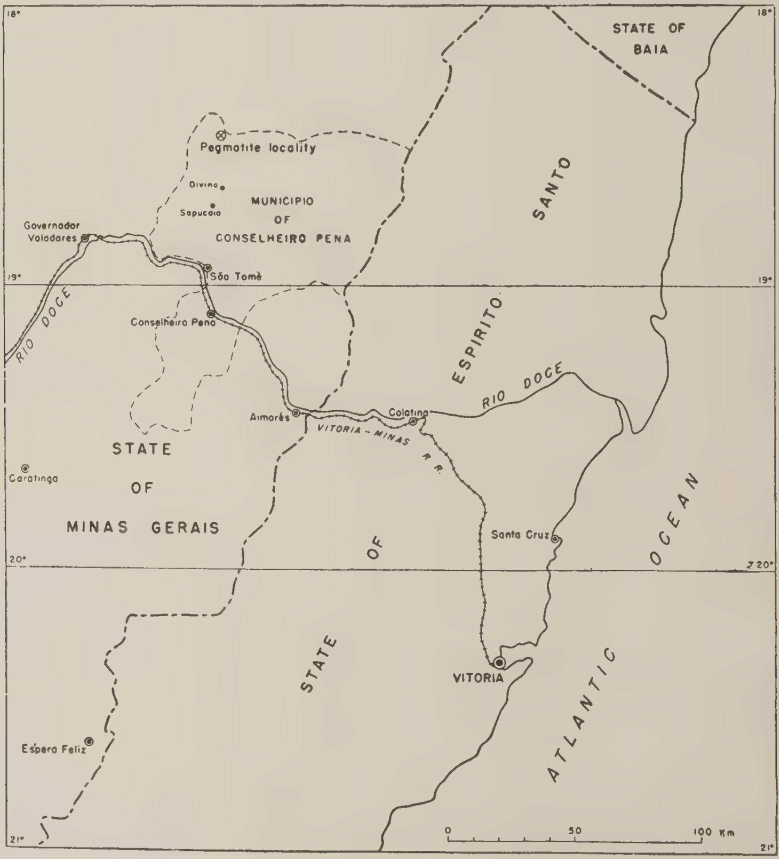

Fig. 1. Index map of a part of southeastern Brazil showing the location of the Corrego Frio pegmatite in the municipio of Conselheiro Pena, eastern Minas Gerais, Brazil.

São Tomé—a small town in the Rio Doce Valley connected by the Victoria-Minas Railroad with the cities of Victoria and Belo Horizonte. The pegmatite locality, 65 km. distant by horse trail from São Tomé, is on a steep slope south of the divide between the municipios of Conselheiro Pena and Mantena, at the head of Corrego Frio, a small tributary in the Rio Doce drainage system. Godoy (1945) has described its location in detail.

HISTORY

In 1942 a clear, greenish-yellow gem crystal was discovered at the Corrego Frio locality and was erroneously believed to be gem beryl or chrysoberyl. In the hope of recovering suitable material for semiprecious gems, approximately 80 cubic meters of material was excavated in 1943. The cleavability and relative softness of the crystals recovered led the miners to believe that they were recovering weathered specimens, and they later drove two short adits into unweathered pegmatite. Mining operations ceased in 1943 after it was established that the unknown mineral was by nature too soft and fragile for gem purposes. Since the discovery of the locality, crystals became distributed widely in eastern Minas Gerais. The mineral was subsequently described as brazilianite, a new sodium aluminum phosphate, by Pough and Henderson (1945).

In late 1944, E. R. Swoboda, an American mineral dealer, aware of the rarity of the crystals, obtained a lease on the locality and supervised additional excavation of the pegmatite. In 1945 and 1946 Mr. Swoboda offered brazilianite crystals for sale to mineral museums, mineral dealers, and mineral collectors in the United States.

The pegmatite locality was visited by the senior author (WTP) in June 1945 in connection with geological studies of the pegmatites of eastern Minas Gerais. To the suite of specimens collected on this visit Mr. Swoboda generously donated a number of his choice specimens for mineralogical study.

REGIONAL GEOLOGY

Eastern Minas Gerais is for the most part underlain by dark-colored schist and gneiss, light-colored granitoid gneiss, and sericitic quartzite. All of these rocks are assigned by Brazilian geologists to the pre-Cambrian. They contain thousands of granitic pegmatites, about 500 of which have been mined successfully for mica, beryl, tantalite and columbite, feldspar and kaolin, and gem stones. Pegmatite mining is one of the principal industries of eastern Minas Gerais. The general geology of the region and the detailed geologic features of the commercially significant pegmatites are described by Pecora and others (U. S. Geol. Survey Bulletin, in preparation).

The Corrego Frio Pegmatite

The pegmatite exposed at the head of Corrego Frio strikes approximately east-west, dips steeply to the north, and is a tabular mass essentially in alignment with the schistosity of the biotite-garnet schist containing it. The pegmatite (Fig. 2) is exposed for about 18 meters on the surface and about 10 meters vertically. Its thickness ranges from three meters at the surface to one and one-half meters in the lower cross-cut adit shown in Fig. 2. A second pegmatite, probably similar to the one described in this paper, is partly exposed in the stream bed about 100 meters to the south.

On the basis of texture and mineral composition, the pegmatite can be subdivided into three units, named, from border to center (1) the massive border zone, (2) the crystal cavity zone, and (3) the quartz lens. Each of these units, illustrated in Fig. 2, is described below.

The massive border zone is exposed on both margins of the pegmatite where its contact with wall-rock schist is regular and well defined. At the surface (see sketch B-B′) the two border units are equal in thickness, and together they make up about two thirds of the thickness of the pegmatite. In the lower adit the unit on the north side (hanging wall) is thicker, but the two units make up the same proportion of the pegmatite. In thickness the unit ranges from 30 cm. to one meter. The border zone is composed principally of massive albite and subordinately of quartz and muscovite. The cleavage faces of the albite are as much as 15 cm. wide. Thin, elongate, blue-green masses (scorzalite and souzalite), up to 25 cm. long, extend across the zone normal to the contact.

The crystal cavity zone has an irregular, poorly defined contact with the massive border zone. It ranges in thickness from a few centimeters, where it lies adjacent to the quartz lens, to one meter, where it comprises the central part of the pegmatite. This zone, in its thickest part and particularly near the edges of the quartz lens, is characterized by irregular vugs and crystal cavities bordered by stubby, terminated quartz crystals, well formed brazilianite crystals, and rhomboid masses of limonite-stained muscovite. Cleavelandite and porous and massive albite all occur in this zone, and in general, a higher proportion of quartz and muscovite occur here in the pegmatite.

The quartz lens has been almost entirely removed by mining. According to the miners, it was originally exposed on the surface for about 5 meters along the strike, where it had an estimated thickness of between one-half and one meter, and gradually thinned to disappear at a depth of about 4 meters. The lower edge of the lens was irregular and had a perceptible rake to the east. The unmined portion of the quartz lens, shown in Fig. 2, is bordered by a mixture of cleavelandite and muscovite.

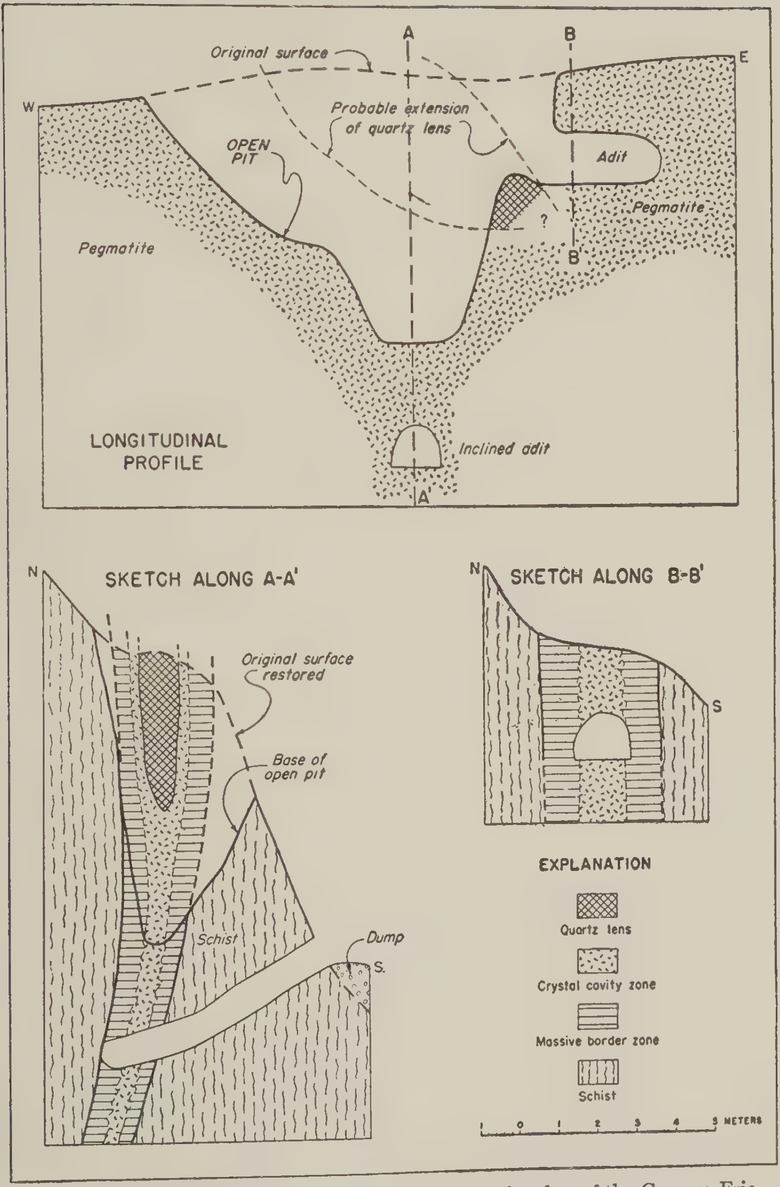

FIG. 2. Longitudinal profile and two cross-section sketches of the Corrego Frio pegmatite showing its zoning and structural relations.

DESCRIPTIVE MINERALOGY

Minerals in the pegmatite

Albite, muscovite, and quartz make up more than 99 per cent of the pegmatite. Six phosphate minerals are present including scorzalite and souzalite—two new hydrous iron magnesium aluminum phosphates; brazilianite, a hydrous sodium aluminum phosphate first described in 1945; blue-green apatite; and two unidentified phosphate minerals. Tapiolite and zircon are rare accessory minerals. Beryl and tourmaline, found in the stream bed below the pegmatite, are not present in the mineral collection studied, nor were they observed in the exposed parts of the pegmatite.

Scorzalite

Scorzalite (scor′-za-lite) is named after Dr. Evaristo Pena Scorza, chief mineralogist of the Departmento Nacional da Produção Mineral, Rio de Janeiro, Brazil. It is dark blue, massive, and occurs principally in the border zone and outer margin of the crystal cavity zone. The largest mass of scorzalite observed is about 7 cm. across, and the masses are rarely free from admixed souzalite.

The physical properties of scorzalite are given in Table 1 and its chemical analysis in Table 2. The analysis gives the formula $(Fe'', Mg) Al_2(PO_4)_2(OH)_2$, with $Fe:Mg=2:1$. This formula, which may also be written $(Fe, Mg) O \cdot Al_2O_3 \cdot P_2O_5 \cdot H_2O$, is analogous to that of lazulite. The two minerals are similar in appearance and have, as shown in Fig. 3, identical *x*-ray powder diffraction patterns. They form a complete isomorphous series which is now under detailed investigation by the authors. It is here proposed that the series be characterized by the two names lazulite (Mg dominant) and scorzalite (Fe dominant). Intermediate members are named by the use of adjective modifiers. Thus the scorzalite from Corrego Frio might be termed magnesian scorzalite.

Scorzalite has higher indices of refraction and higher specific gravity than lazulite, as shown in Table 1 by a comparison of lazulite $(Mg:Fe=8:1)$ from Chittenden, Vt. (Palache and Gonyer, 1930) with scorzalite from Corrego Frio $(Mg:Fe=1:2)$.

Souzalite

Souzalite (sōze′-a-lite) is named after Dr. Antonio José Alves de Souza, former Director of the Departamento Nacional da Produção Mineral, Rio de Janeiro, Brazil. The mineral is green and occurs in irregular, fibrous masses so intimately associated with scorzalite that it is believed

TABLE 1. PHYSICAL PROPERTIES OF SCORZALITE AND SOUZALITE FROM MINAS GERAIS, AND LAZULITE FROM CHITTENDEN, VT.

	Scorzalite	Souzalite	Lazulite
Color (hand spec.)	dark blue	dark green	dark blue
Habit	massive	coarse fibrous aggregate	massive
Specific gravity	3.268 (pycnom.)	3.087 (pycnom.)	2.96
Hardness	6	$5\frac{1}{2}$–6	5–6
Crystal system	Monoclinic	Monoclinic (?)	Monoclinic
Indices of Refraction			
Na (±0.002) X	1.633 (colorless)	1.618 (green)	1.604 (colorless)
Y	1.663 (blue)	1.642 (blue)	1.633 (blue)
Z	1.673 (blue)	1.652 (yellow)	1.642 (blue)
2V	62° (calc.)	68° (calc.)	64° (calc.)
Optical character	(−)	(−)	(−)
Dispersion of the optic axes	$r<v$, percept.	$r>v$, extreme and symmetrical	$r<v$, percept.
Twinning	multiple	polysynthetic twins, max. extinction 12°; comp. pl. parallel to good cleavage	
Cleavage	good	one good cleavage, approx. at right angle to fair cleavage	Good
Orientation	$Y=b$ X near *c*	X⊥cleavage plates; Z=elongation (near c?)	

to be a hydrothermal alteration product of scorzalite. The largest mass of souzalite observed is 10 cm. across.

The physical properties of souzalite are given in Table 1 and its chemical analysis and formula in Table 2. Souzalite, like scorzalite, is a hydrous magnesium iron aluminum phophate but its formula is of a different type: $(Mg, Fe'')_3(Al, Fe''')_4 (PO_4)_4 (OH)_6 \cdot 2H_2O$. The *x*-ray powder pattern of souzalite (shown in Fig. 3 and in Table 3) does not resemble any of about 25 phosphate minerals with which it has been compared.

Because the type souzalite from the Corrego Frio pegmatite occurs as

TABLE 2. CHEMICAL ANALYSES AND MOLECULAR RATIOS OF SCORZALITE AND SOUZALITE FROM MINAS GERAIS, BRAZIL

(J. J. Fahey, *analyst*)

	Scorzalite				Souzalite			
	Per cent	Ratio			Per cent	Ratio		
Al_2O_3	30.87	.3028	.3073	0.98	26.07	.2557	.2732	2.04
Fe_2O_3	.54	.0034			2.65	.0166		
TiO_2	.10	.0011			.07	.0009		
FeO	14.74	.2051	.3140	1.01	11.49	.1599	.4036	3.00
MgO	4.23	.1049			9.62	.2386		
MnO	.11	.0015			.31	.0044		
ZnO	.17	.0021			none	—		
SnO	none	—			.04	.0003		
CaO	.02	.0004			.02	.0004		
P_2O_5	42.90	.3022	.3022	0.97	37.70	.2656	.2656	1.98
H_2O-	none				none			
H_2O+	5.86	.3252	.3252	1.04	12.04	.6681	.6681	4.98
Total	99.54				100.01			
Formula	$R_2O_3 \cdot RO \cdot P_2O_5 \cdot H_2O$				$2R_2O_3 \cdot 3RO \cdot 2P_2O_5 \cdot 5H_2O$			
Mol. ratio	MgO:FeO=1:2				MgO:FeO=3:2			

Note: In the blowpipe flame, both minerals are infusible and disintegrate. Both minerals are soluble with difficulty in HCl.

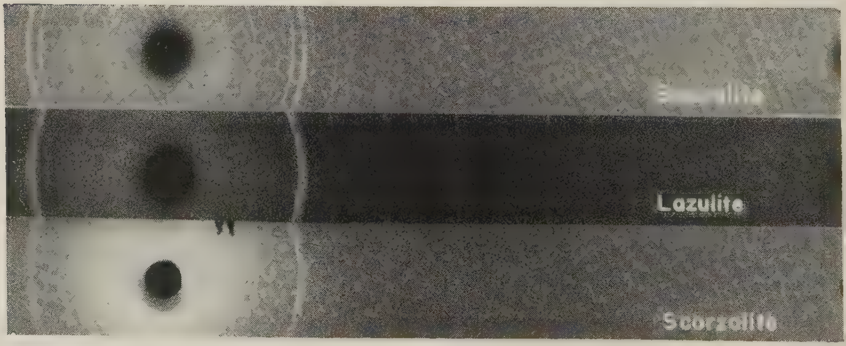

FIG. 3. X-ray powder diffraction photographs of scorzalite and souzalite from the Corrego Frio pegmatite, Minas Gerais, and of lazulite from Graves Mt., Georgia.

coarse, fibrous, twinned aggregates, the optical constants given in Table 1 are less reliable than those determined for scorzalite. The powdered mineral in immersion shows positive elongation, one very good cleavage normal to the Bx_a and a diagnostic dispersion of the optic axes.

TABLE 3. MEASURED *d* SPACINGS OF *X*-RAY POWDER PATTERN PHOTOGRAPH OF SOUZALITE FROM THE CORREGO FRIO PEGMATITE

(Filtered Cu radiation, $\lambda = 1.5418$ Å)

Legend: VS = very strong; S = strong; M = medium; MW = medium weak; W = weak; F = faint; B = broad.

(measurements by E. A. Cisney)

Å	Intensity	Å	Intensity
(3) 5.35	S	1.665	F
(2) 3.79	S	1.629	MW
3.57	F	1.574	W
3.25	W	1.530	MW
2.852	W	1.511	W
(1) 2.690	VS	1.448	MW
2.505 2.472 2.436	S	1.418	F
		1.376	F
		1.348	W
2.324	M	1.320	MW
2.246	F	1.228	MW
2.027	S	1.218	W
1.920	F	1.183	F
1.894	W	1.169	F
1.868	W	1.015	MB
1.794	F	.898	WB

Brazilianite

The mineralogy of brazilianite from this locality has been described by Pough and Henderson (1945), Tavora (1945), and Hurlbut and Weichel (1946). A second occurrence of brazilianite in the Palermo pegmatite, North Groton, N. H., has been described by Frondel and Lindberg (1948).

George Switzer of the U. S. National Museum, Washington, D. C., examined thirty-seven new crystals from the Pecora-Swoboda collection. The crystals are all splendent, range in size from one-half to four centimeters across, and range in weight from less than one up to thirty-two grams. The most completely developed crystals are doubly terminated and have 20 to 30 faces. Switzer (personal communication) states: "The crystals have two habits, as described by Pough and Henderson (1945). The dominant habit is one with a narrow prism zone and considerable elongation parallel to [100]. This habit is similar to that recently described for brazilianite from New Hampshire by Frondel and Lindberg (1948). In the less common of the two habits the prism zone is slightly elongated. No new forms were noted in the Brazilian crystals."

According to available sources of information, about 30 kg. of gem crystals and about 200 kg. of specimen "pound material" were recovered in the period 1943–46. Many of the gem crystals were destroyed in preparation for or during lapidation. According to two miners, one large many-faced crystal recovered in 1943 weighed about two kilograms and was broken up in an attempt to acquire gem-clear pieces. The largest crystal known to exist weighs approximately one kilogram and is on display in the U. S. National Museum in Washington. About a dozen other crystals are known whose weights range from 100 to 1,000 grams. Most of the crystals are less than an inch across and weigh less than 10 grams.

The indices of refraction for brazilianite, as determined from a number of specimens, are higher by 0.003 than those published by Pough and Henderson (1945), as shown below:

	Earlier data (published)	New data (± 0.001, Na)
nX	1.598	1.601
nY	1.605	1.608
nZ	1.617	1.620

Other minerals

Apatite occurs as dark-green, hexagonal crystals up to 3 cm. across, commonly clear or gemmy in quality. As indicated by its indices of refraction ($\omega = 1.633$ and $\epsilon = 1.630$), the mineral is probably a nearly pure fluorapatite.

Two unidentified phosphate minerals were noted in a few specimens. One, a light-brown mineral, occurs as an irregular intergrowth with altered scorzalite and its optical constants are: biaxial (+), $2V = 50°$ (estimated); $r < v$, strong; $nX = 1.607$, $nY = 1.619$, $nZ = 1.632$; color in immersion is yellow. The second unidentified phosphate mineral occurs as dark-brown prismatic crystals in tiny alteration cavities in the light-brown phosphate mineral or in scorzalite. Its optical constants are: biaxial (+), $2V = 20°$ (estimated); $nX =$ (yellow-brown) $= 1.705$, $nY =$ (dark-yellow) $= 1.709$, $nZ =$ (yellow) $= 1.735$; orientation, $X =$ elongation; orthorhombic (?).

Tiny bipyramidal crystals of colorless zircon with the prism form subordinately developed are imbedded in a quartz-albite mixture and surrounded by the unidentified light-brown phosphate mineral.

Black, splendent, striated, tabular crystals of tapiolite are imbedded in albite in a few specimens. The crystals range up to one centimeter in length. Its optical constants are: Uniaxial (+); birefringence, very high; ω (brownish-red) and ϵ (greenish) both higher than 2.0 (selenium melt); Absorption E > O, strong.

GENESIS

The well defined contact with schist and the texture of the border facies support the hypothesis of intrusion of a magmatic fluid which consolidated from border to center after emplacement. Similar relations exist for hundreds of other pegmatites in the region in many different kinds of host rock. Accessory phosphate minerals are common in many pegmatites near the Corrego Frio locality, but are rare in pegmatites of other districts in Minas Gerais. Within the granitic petrogenetic province of eastern Minas Gerais, with a locus in Conselheiro Pena, is a subprovince characterized by a relatively significant concentration of P_2O_5. With respect to other pegmatites in this subprovince, the Corrego Frio pegmatite is especially characterized by the presence of the rare phosphate minerals brazilianite, scorzalite, and souzalite, and by the conspicuous absence of potash feldspar.

The sequence of mineral formation in the pegmatite has not been established with certainty. The massive albite is characteristic of the early stage of pegmatite consolidation, whereas cleavelandite has formed in the late stage. Scorzalite, souzalite, and apatite are intermixed with massive albite in the border zone and are included by crystals of brazilianite and quartz in the crystal cavity zone. Shell-like intergrowths of apatite and massive albite in the outer margin of the crystal cavity zone indicate that apatite began to form near the end of massive albite formation. The field relations support the hypothesis of continuous crystallization from a magmatic to an autohydrothermal stage.

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LUDLAMITE FROM THE PALERMO MINE, NORTH GROTON, NEW HAMPSHIRE

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Boston University, Boston, Mass.

Abstract

Ludlamite, hydrous iron phosphate, has been found in crystals in small veins and in large masses in triphyllite at the Palermo mine, North Groton, New Hampshire.

Powder pictures of the Palermo material are identical with those of the type Cornwall material and of the Hagendorf, Bavaria lehnerite. Rotation and Weissenberg pictures about [010] and [001] give: Space group $P2_1/a$; a_0 10.48±0.06, b_0 4.63±0.05, c_0 9.16±0.06, $\beta=100°36'$; $a_0:b_0:c_0=2.26:1:1.98$. Cell volume and G. 3.14 measured on 10 crystals give M_0 833.1. An analysis by Gonyer of Palermo ludlamite gives $Fe_6(PO_4)_8\cdot 8H_2O$ in the unit cell with molecular weight of 859.3.

Opt.: Biaxial (+); 2V 80°; $\alpha=1.650$; $\beta=1.667$; $\gamma=1.688$. $r>v$ slight.

The little known iron phosphate, ludlamite, has recently been discovered amongst the interesting phosphate pocket minerals in the Palermo Mine of North Groton, New Hampshire. The original find was made by Mrs. Leland Wyman and was transmitted to the author by Dr. Wyman for study. Although the first material was very limited in quantity, the Wymans kindly offered all of it for study.

Occurrences

The first find of ludlamite at Palermo was as crystals in narrow veinlets in the triphyllite, which is the primary phosphate of the pegmatite. The largest diameter of the crystals was about 2 mm. In small cavities within the veinlets additional phosphates are found coating the ludlamite. The first of these is *fairfieldite* which occurs as white sheaf-like aggregates. *Vivianite* occurs on the fairfieldite as separate crystals, flattened on *b* and elongated parallel to *c*. One of the vivianite crystals was 4 mm. long. Coating the vivianite was a *white fibrous mineral* with high birefringence, the indices ranging between 1.615 and 1.71 approximately. 2V is about 80° and the optical sign is positive (+). It may well be a new mineral, but there was insufficient material available for further study. *Reddingite* occurs in very small crystals on the ludlamite. Some yellowish orange bladed crystals with three triclinic pinacoids were implanted on the reddingite and were measured, but because of lack of material they were not subject to adequate study. They may well represent the incompletely described mineral *stewartite.*

In a trip made by the author to the Palermo quarry this past summer in company with Dr. Frondel, a large newly exposed altered triphyllite pocket was discovered in which large quantities of massive ludlamite were found capping and penetrating the triphyllite. The sequence of mineralization in the massive material was essentially the same as that described in the veins. The *triphyllite* is altered to *ludlamite*, frequently forming crystals 5 mm in greatest dimensions. The best ludlamite crystals usually occur in a matrix of powdery white *fairfieldite* which is later than the ludlamite. *Siderite* is the next alteration product; it occurs in crystallized rhombs and in a very light brown massive form. The triphyllite, in many sections several inches across, is completely replaced by siderite. Dark blue massive *vivinanite*, which is probably later than the siderite, is sparsely distributed through the altered portions of the triphyllite. The end stage of alteration of the triphyllite is *wad*. Pyrite and arsenopyrite are frequently present in small amounts.

CRYSTALLOGRAPHY

Five well formed crystals were measured, yielding data which are so similar to those of the original description of Maskelyne and Field (1877) that nothing further need be added here. The best crystals are complete counterparts of that figured in Dana (1892).

UNIT CELL

Powder pictures were taken of the type ludlamite from Cornwall, of the Palermo ludlamite, and of the lehnerite from Hagendorf, Bavaria. They proved identical. Berman (1925) concluded that lehnerite and ludlamite are identical on optical and physical grounds, and the identification is herewith confirmed.

Rotation and Weisenberg pictures were taken about the [010] and [001] axes, with the following results: Space group $P2_1/a$; a_0 10.48 ± 0.06, b_0 4.63 ± 0.05, c_0 9.16 ± 0.06; $\beta = 100°36'$; $a_0{:}b_0{:}c_0 = 2.26{:}1{:}1.98$. The elements of Maskelyne and Field (1877) were $a{:}b{:}c = 2.2520{:}1{:}1.9819$; $\beta = 100°33'$.

CHEMISTRY

The precise chemical formula of ludlamite has been in doubt since the first analysis by Flight in Maskelyne and Field (1877), which indicated that the mineral was a basic hydrated iron phosphate. The analysis of Mullbauer (1925) indicated once more the basic hydrated character of the mineral, but there was less water and also a substitution of manganese and magnesium for iron in comparison with the earlier analysis. The x-ray examination of the mineral indicated that the unit cell could not possibly house the complicated formulae listed for ludlamite and lehnerite, and a simple hydrate of iron phosphate with isomorphous replacement of manganese and magnesium for iron was predicted.

An analysis of the Palermo ludlamite by Mr. Forrest Gonyer indicates that the early analyses can be regarded with considerable suspicion. Hydrated phosphates frequently yield analyses showing considerable variation, particularly in the phosphorus pentoxide and water content, from the theoretical formula. That this is true may be seen in Table 1 where the analysis by Gonyer is given in column 1. Ten determinations of the *specific gravity* of the Palermo material gave a rather consistent value of 3.14. This density, coupled with the cell volume obtained from *x*-ray analysis, gives a cell weight of 833.08, and the composition of the unit cell may be calculated as in column 6. Column 5 gives the composition for the theoretical composition of $Fe_3(PO_4)_2 \cdot 4H_2O$ which is in satisfactory agreement with the analysis by Gonyer.

TABLE 1. ANALYSES AND CHEMICAL COMPOSITION OF LUDLAMITE

	1.	2.	3.	4.	5.	6.		7.		8.	9.
FeO	49.22	49.59	45.91	52.76	50.17	5.75	5.95	5.41	6.25	6.09	6
MnO	—	—	3.10	—	—	—		.37			
MgO	0.96	0.97	2.21			0.20		.47			
P_2O_5	32.95	33.20	33.87	30.11	33.06	1.95		2.02		1.76	2
H_2O	16.12	16.24	14.91	16.98	16.77	7.51		7.00		7.82	8
Insol.	.57										
Total	99.85	100.00	100.00	99.85	100.00						

1. Weight percentages—Palermo ludlamite—analyst Gonyer.
2. Weight percentages of "1" recalculated to $=100\%$.
3. Weight percentages Hagendorf "lehnerite"—analyst Mullbauer.
4. Weight percentages Cornwall ludlamite—analyst Flight.
5. Weight percentages theoretical formula $Fe_3(PO_4)_2 \cdot 4H_2O$.
6. No. of molecules in unit cell of "2"; $M_0=833.08$, S.G.$=3.14$ (meas.).
7. No. of molecules in unit cell of "3"; $M_0=846.34$, S.G.$=3.19$ (meas.).
8. No. of molecules in unit cell of "4"; $M_0=827.77$, S.G.$=3.12$ (meas.).
9. No. of molecules in unit cell of "5"; $M_0=859.25$, S.G.$=3.24$ (calc.).

If the cell contains two molecules of this composition, the cell molecular weight would be 859.25, which is substantially higher than the value of 833.08 calculated for the Palermo material. The calculated specific gravity for the theoretical formula based on the cell volume and a cell weight of 859.25 is 3.24 which is about 3% higher than the measured 3.14. This discrepancy is higher than the usual experimental error and must be ascribed to physical factors, such as the excellent basal cleavage; or to chemical factors such as partial leaching of phosphoric acid or incomplete hydration of the mineral with definite omission of some of the water molecules in the structure.

There seems to be little doubt that the composition is $Fe_3(PO_4)_2 \cdot 4H_2O$. Ludlamite, therefore, must be grouped with hopeite, parahopeite, anapaite, and phosphophyllite. A comparison of phosphophyllite (Wolfe, 1940) and ludlamite indicates the similarity in crystallographic properties.

	Ludlamite		*Phosphophyllite* (Wolfe, 1940)
a_0	10.48	c	10.49
b_0	4.63	b	5.08
c_0	9.16	a	10.23
β	100°36′	β	120°15′
Cell volume	437.7		470.92
Space Group	$P2_1/a$		$P2_1/a$ in ludlamite orientation
Cleavage	{001} perfect		{100} perfect = {001} in ludlamite orientation
Cell contents:	$Fe_6(PO_4)_4 \cdot 8H_2O$	Cell contents:	$Zn_4(Fe, Mn)_2(PO_4)_4 \cdot 8H_2O$

The habit of both species is entirely comparable; although twinning which is so common in phosphophyllite is lacking in ludlamite. The larger cell of phosphophyllite can be ascribed to the greater ionic radius of the zinc which forms two thirds of the cation content.

The thermal analysis curve for ludlamite shows one sharp endothermic reaction at a temperature of 335° C., a much smaller similar reaction at 545° C., a small exothermic reaction at 625° C., and a very small endothermic reaction at 935° C. The 335° C., endothermic reaction undoubtedly is the result of the loss of water. The other minor breaks have not been explained, but it is doubtful whether either of the two other small endothermic breaks can represent a loss of hydroxyl, which was required by the earlier analyses.

Optics

n	
$\alpha = 1.650$	Biaxial positive (+)
$\beta = 1.667$	$r > v$ slight
$\gamma = 1.688$	

Acknowledgment. The facilities of the Berman laboratory in the Department of Mineralogy at Harvard were made available to the author during the course of this investigation for which he is highly grateful. The excellent analysis by Mr. Forrest Gonyer and the thermal analysis by Dr. Clifford Frondel are much appreciated.

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A FLUORESCENCE STUDY OF WYOMING BENTONITE

Bahngrell W. Brown, *University of Wyoming, Laramie, Wyoming.*

Abstract

It was found that a water solution of zinc uranyl acetate upon contacting certain clays such as Wyoming swelling bentonite and Colorado beidellite caused them to fluoresce under the ultraviolet light, whereas other clays such as attapulgite and illite do not so respond. It was noted that there were appreciable differences in effect with several Wyoming clays of the bentonite family. An experiment was set up to determine whether or not this difference in effect was a truly measureable quantity and if it could be correlated with the known physical properties of the bentonitic clays. Results indicated a qualitative field test based on the technique.

Introduction

It was noted in the course of research on Wyoming clays that a water solution of zinc uranyl acetate upon contacting the swelling bentonites (hydrophilic clays) caused them to immediately fluoresce in a short gamma ultra-violet radiation; whereas, other clays, such as kaolin, did not so fluoresce when equally treated, and that members of the bentonite family characterized as non-swelling bentonites (inaptly called fuller's earths) fluoresced but slightly or not at all.

It was the purpose of this study to determine if the difference in the intensity of the effect experienced with various swelling clays was a measurable quantity, and whether or not it could be correlated in any way with the known physical properties of the clay determined by standard clay testing methods.

Procedure

The samples used in this study were picked at random from clays previously studied at the Natural Resources Research Institute and reported in its No. 2 Bulletin (1). The fluorescent agent used was a water solution of zinc uranyl acetate prepared after the manner of a sodium determination (2), and checked under the ultraviolet light for negative fluorescence by placing a drop of solution on diatomaceous earth.

The technique used was as follows: Approximately 5 grams of each dry clay sample, prepared as for bentonite testing, were placed in uniform porcelain crucibles. The sample numbers were marked on the under side of the crucibles so as not to be known by the operator while making the test. Next, the crucibles were shuffled and assigned a letter for reference. The samples were checked for negative fluorescence and a single drop of the zinc uranyl reagent was placed on each sample. The intensity of fluorescence for each sample was rated on the basis of 10 with the strongest being assigned that numerical value, and the others correspondingly relative values. The sample numbers were then determined and the numerical fluorescence value reassigned to its respective sample.

The contaminated spot was removed, the samples again checked for residual fluorescence, again shuffled and a second run was made using two drops of reagent on each clay. This procedure was then repeated a third time with a third shuffle, using three drops of reagent.

The results of all three tests were averaged for each clay and this was used as a basis for correlation with the physical properties of each.

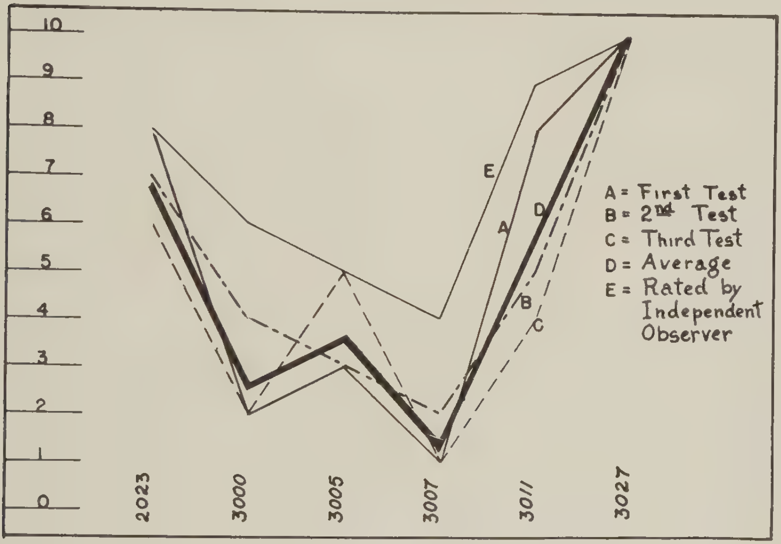

FIG. 1

REPRODUCIBILITY

Six samples picked at random from the clays reported (1) were treated by the zinc uranyl technique. The results were graphed in Fig. 1. Curve *E* is the intensity curve as reported by an independent observer who had no previous knowledge of the study. The relative agreement was found to be good between extremes but not reliable for small differences. It is anticipated that with further practice in the technique and averaged observations closer reliability can be attained. The reliability found would be sufficient for a field test concerned with rapid determination of bentonitic deficiencies.

CORRELATION WITH KNOWN PHYSICAL PROPERTIES

A resume of the predetermined physical properties of the zinc uranyl studied clays was made to learn whether or not the technique could be applied as a rapid field test for these properties. The results of this resume are reported in graphic form in Fig. 2.

It will be seen from Fig. 2 that there is a definite correlation trend between the zinc uranyl test and the properties of green compressive strength, viscosity, and initial gell strength (shear). It will also be noted that the agreement is not entirely consistent for major differences but has sufficient reliability in its correlation with green strength properties and viscosity to indicate these in a qualitative way.

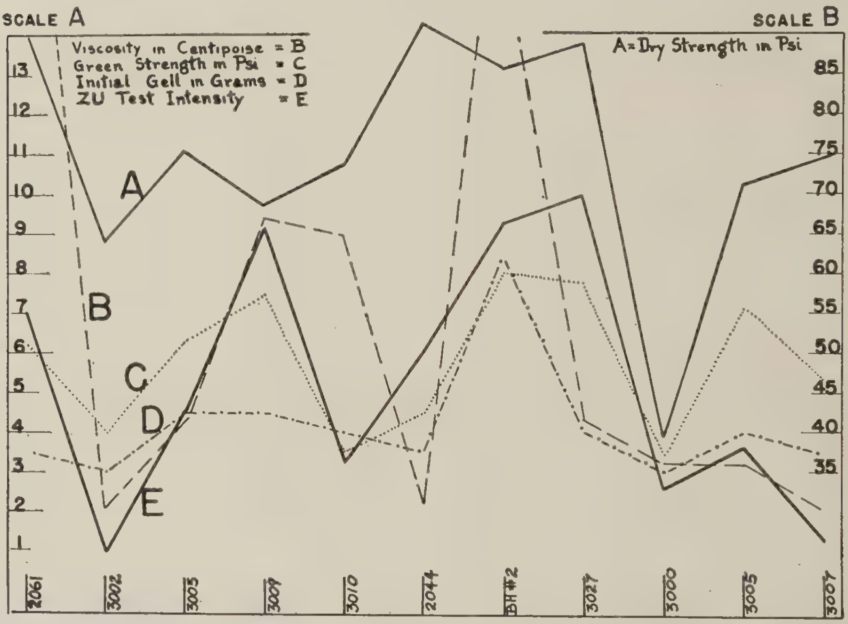

FIG. 2

THEORY

It is doubtful if lattice substitution (as measured by base exchange capacity) is operative in this effect. It was thought at first that uranyl ions might enter into base exchange forming hydrophobic fluorescent salts at the interface. This thought was abandoned when it was found that attapulgite, illite, and kaolinite which have appreciable base exchange capacities (3) did not enter into the effect.

It is, also, doubtful if capillarity (Van der Waal's adsorption) has any influence on the effect. Diatomaceous earth, a highly adsorptive capillary medium, does not respond to zinc uranyl treatment.

A more reasonable explanation is to be found in the dehydrating powers of the clay involving free energy levels of the order chemisorption. Grim has held that the swelling of the montmorillonite is motivated by expansion in the lattice of discrete hydrates (4). Whether or not the hydrates are discrete, it is generally believed that the swelling properties of the bentonites are due to interplanar hydration of one sort or another between the silicate layers (5).

The part the sodium ion plays in this effect was not determined but it may prove to be considerable.

If there is adequate spacing in the lattice, hydration may proceed without consequent swelling. Colorado's pink beidellite is a non-swelling member of the montmorillonite group with a comparable structure (6). As would be expected, beidellite responds to this test with beautiful fluorescence, whereas Florida fuller's earth (attapulgite), halloysite, and the very platey illite do not. These later three clays are representatives of distinct groups and are considered structurally different from clays in the montmorillonite-beidellite group (7).

Conclusions

It is concluded from the results here shown that a quick qualitative field test could be designed, involving the interfacial dehydration of zinc uranyl acetate and ultra violet fluorescence of the anhydrous salt. This test would roughly estimate certain physical properties of the *swelling* bentonites which would normally require lengthy laboratory procedures, and with a degree of accuracy that should be adequate for field work.

References

(1) H. Fisk, "Bentonite," *University of Wyoming Natural Resources Research Institute,* Bulletin No. **2** (1946).
(2) Snell and Biffen, "Commercial Methods of Analysis," p. 223.
(3) R. E. Grim, *Ill. State Geol. Surv.,* **R.I. 80,** 251.
(4) *Ibid.,* p. 242.
(5) *U. S. Geol. Survey,* Professional Paper, **205-B,** 52.
(6) *Ibid.,* pp 44, 45.
(7) R. E. Grim, *Ill. State Geol. Surv.,* **R.I. 80,** 231–234.

THE WATHENA, DONIPHAN CO. KANSAS, METEORITE*

E. P. Henderson, *Associate Curator, Mineralogy and Petrology, U. S. National Museum* and Stuart H. Perry, *Associate in Mineralogy, U. S. National Museum.*

This small but rather well rounded iron of 566 grams was found in September 1939 in a ditch next to a country road running northwest from Wathena, Kansas, and about one mile from that town, by Mr. Russell C. Maag. The Latitude is 39° 49′ N. and the Longitude is 94° 55′ W. It was sent to the U. S. National Museum for identification and shortly thereafter acquired and added to the Roebling Collection.

Mr. Maag reported that an exceptional fine meteor display was witnessed in Doniphan County, Kansas, in August of 1939 and suggested that perhaps this iron fell at that time. Since the surface of the Wathena iron is totally without flight markings or anything that can be identified as belonging to the original crust, it is unlikely that this iron fell at that time. In all probability it is an old fall.

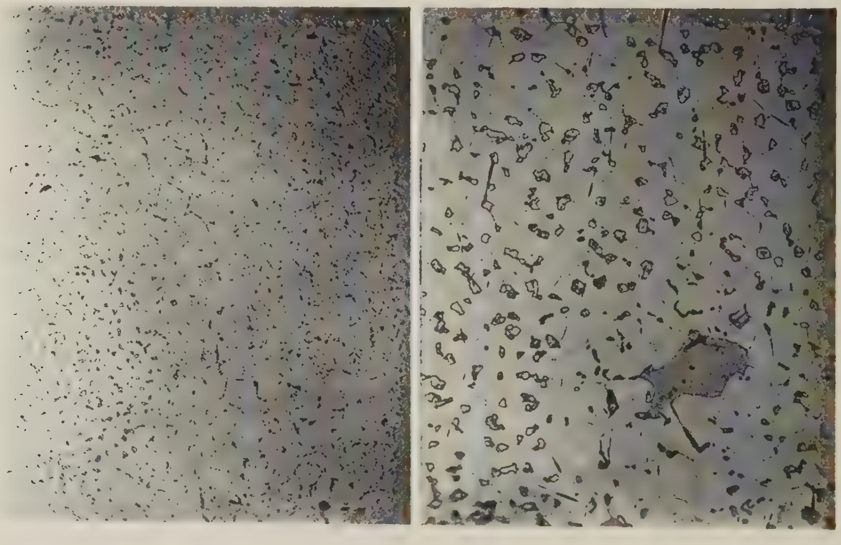

Fig. 1. Characteristic general structure. Uniform dispersal of phosphide particles; the area at the right shows kamacite grain boundaries with large phosphide bodies located along those boundaries; the left shows coarser phosphide particles. Picral 10 sec. 66 mag.

Fig. 2. A large schreibersite mass surrounded by an area of fine granulation and phosphide particles along grain boundaries. There is no indication of any diffusion of the phosphide bodies by reheating. Picral 10 sec. 170 Mag.

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A small slice was made, etched and carefully examined, to obtain for the analysis, a section that would be typical of the structure of the meteorite.

WATHENA KANSAS, METEORITE

E. P. Henderson, *analyst*

Fe	93.51
Ni	5.56
Co	.60
P	.27
S	.11
Insol.	.02
	100.07

$$\text{Mol. Ratio } \frac{\text{Fe}}{\text{Ni and Co}} = 16.07$$

The metallographic structure of this meteorite is that of the nickel poor ataxites with granular kamacite and small schreibersite bodies rather uniformly scattered through the mass, but these bodies are essentially located between the granules of kamacite. In areas where the phosphide particles are most numerous the kamacite granules are smallest. The schreibersite inclusions are all irregular in shape and without small protruding spines.

The structure, composition, and molecular ratio agree with other low nickel ataxites. A characteristic feature of this iron is the general absence of easily discernible grain boundaries in the kamacite and the uniform distribution of the schreibersite particles.

SVANBERGITE FROM NEVADA[1]

GEORGE SWITZER, *U. S. National Museum, Washington, D. C.*

ABSTRACT

Svanbergite, $SrAl_3(SO_4)(PO_4)(OH)_6$, has been found for the first time in North America near Hawthorne, Nevada. It has the following properties: Point group $\bar{3}\ 2/m$ (?); probable space group $R\ \bar{3}\ m$; unit cell dimensions: $a_0 = 6.99$ Å, $c_0 = 16.75$ Å, Specific gravity = 3.22. Optical properties: uniaxial (+), $\omega = 1.635$, $\epsilon = 1.649$. Chemical composition: Al_2O_3 36.91%, Fe_2O_3 0.24, CaO 3.25, SrO 12.84, P_2O_5 16.70, SO_3 17.34, H_2O 12.51.

INTRODUCTION

Svanbergite, $SrAl_3(SO_4)(PO_4)(OH)_6$, is a rare member of the alunite group. The locality described here is the first occurrence in North America. Previously known localities are: Horrsjöberg and Westanå, Sweden, and Chalmoux, Soâne-et-Loire, France.

The new locality for svanbergite is the Dover andalusite mine, 12 miles northeast of Hawthorne, Mineral County, Nevada. It was first noted there by Mr. M. Vonsen, of Petaluma, California in 1939. An independent discovery was made by Mr. Edgar H. Bailey of the U. S. Geological Survey in 1944.

The Dover mine is in the foothills of the southwestern end of the Gillis range. It may be reached from Hawthorne over a paved road for six miles to Thorne, and thence six miles east on a dirt road from Thorne.

The svanbergite occurs in well formed crystals imbedded in, or emplanted on, green pyrophyllite. The pyrophyllite is abundant in the andalusite-corundum ore, which has been mined periodically and in small quantities.

The material used in this study was very kindly supplied by Mr. M. Vonsen and Dr. John Peoples, both of Petaluma, California, and is now on deposit in the U. S. National Museum (USNM 105688).

MORPHOLOGY

Svanbergite from Nevada is found in sharp, well-formed crystals ranging in size from less than a millimeter to a maximum of about four millimeters. The smaller crystals are pale yellow in color, while the larger ones are medium reddish brown and often have a lighter colored core. The crystals are always attached to the matrix so that the form development at only one end of the *c* axis can be observed.

The dominant form is the rhombohedron *s* $\{01\bar{1}2\}$, and the resultant habit is pseudo-cubic. This rhombohedron appears either alone, or modified by smaller faces of the basal pinacoid and other rhombohedrons, and rarely by the prism *m* $\{10\bar{1}0\}$. Typical crystals are illustrated in Fig. 1.

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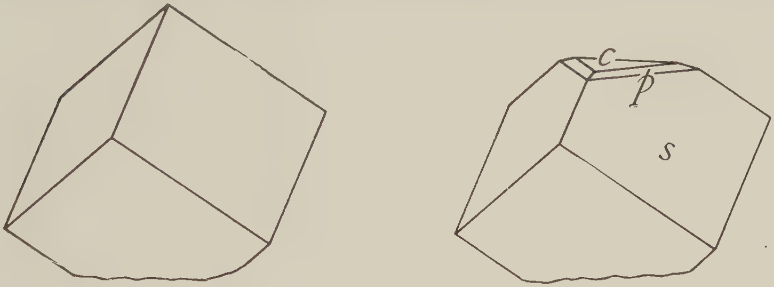

Fig. 1

The morphological data of svanbergite from Nevada are summarized in Table 1. The forms are indexed on the basis of the axial ratio indicated by *x*-ray studies of svanbergite from Sweden by Ygberg[1] and Pabst,[2] as well as those by the writer on Nevada material.

Table 1. Morphological Data of Svanbergite from Nevada

Form	No. of times observed	Quality	ρ		
			Measured range	Weighted mean	Calculated value
c 0001	4	good	0°00′– 0°02′	0°01′	0°00′
m $10\bar{1}0$	2	fair	90°01′–90°05′	90°02′	90°00′
p $01\bar{1}5$	2	fair to poor	28°57′–29°32′	28°57′	28°33′
s $01\bar{1}2$	10	excellent to fair	53°39′–53°43′	53°41′	53°41′
d $02\bar{2}1$	2	poor	79°42′–79°45′	79°43′	79°35′
t $10\bar{1}7$	2	fair to poor	21°26′–21°36′	21°31′	21°14½′
u $10\bar{1}4$	4	fair to poor	34°22′–34°26′	34°24′	34°13½′
e $10\bar{1}1$	3	poor	68°56′–69°50′	69°24′	69°49′

The original descriptions of svanbergite from Sweden and France were made without benefit of *x*-ray studies, hence the dominant rhombohedron was indexed as $\{10\bar{1}1\}$. *X*-ray work shows that the dominant rhombohedron is $\{01\bar{1}2\}$ when the crystal setting is made to correspond to the rhombohedral cell. In Table 2 the forms found by previous workers on svanbergite from Sweden and France are correlated with those of the

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[1] Ygberg, E. R., Svanbergite from Horrsjöberg: *Arkiv för Kemi, Mineralogi och Geologi,* **20A,** no. 4, 1–17 (1945).

[2] Pabst, A., Some computations on svanbergite, woodhouseite and alunite: *Am. Mineral.,* **32,** 16–30 (1947).

TABLE 2. SVANBERGITE: CORRELATION OF FORMS

Previous work to Switzer: $0\bar{1}00/00\bar{1}0/\bar{1}000/0002$

Dauber[1] $c=1.2063$	Seligman[2] $c=1.2008$	Lacroix[3] $c=1.2437$	Ygberg[4] $c=1.2111$	Switzer $c=2.3565$
		a' 0001		c 0001
				m $10\bar{1}0$
				p $01\bar{1}5$
r $10\bar{1}1$	$10\bar{1}1$	p $10\bar{1}1$	r $10\bar{1}1$	s $01\bar{1}2$
$4r$ $40\bar{4}1$	$40\bar{4}1$	e^3 $40\bar{4}1$	n $40\bar{4}1$	d $02\bar{2}1$
	$50\bar{5}1$	$e^{11/4}$ $50\bar{5}1$		t $10\bar{1}7$
				u $10\bar{1}4$
	$02\bar{2}1$	e' $02\bar{2}1$	s $02\bar{2}1$	e $10\bar{1}1$

[1] Dauber, H., Ueber Svanbergit und Beudantit: *Pogg. Ann.*, **10,** 579 (1857).

[2] Seligman, G., Mineralogische Notizen II: *Zeit. Krist.*, **6,** 227–229 (1882).

[3] Lacroix, A., Mineralogie de la France, **IV,** 592–595 (Paris, 1910).

[4] *Op. cit.*, Ygberg gives $\rho_{10\bar{1}1}=54°37'$ from which he incorrectly calculates the axial ratio $c=1.2111$. The correct value is $c=1.2194$.

TABLE 3. SVANBERGITE ANGLE TABLE

Hexagonal—R; hexagonal scalenohedral—$\bar{3}\ 2/m$ (?)

$a:c=1:2.3565$; $\alpha=61°44'$; $\rho_0=r_0=2.7210:1$; $\lambda=108°45'$

	ϕ	$\rho=C$	A_1	A_2
c 0001 111	—	0°00′	90°00′	90°00′
m $10\bar{1}0$ $2\bar{1}\bar{1}$	30°00′	90 00	90 00	30 00
t $10\bar{1}7$ 322	30 00	21 $14\frac{1}{2}$	71 43	90 00
u $10\bar{1}4$ 211	30 00	34 $13\frac{1}{2}$	60 51	90 00
e $10\bar{1}1$ 100	30 00	69 49	35 $37\frac{1}{2}$	90 00
p $01\bar{1}5$ 221	−30 00	28 33	90 00	65 33
s $0\bar{1}12$ 110	−30 00	53 41	90 00	45 45
d $02\bar{2}1$ $11\bar{1}$	−30 00	79 35	90 00	31 36
o $05\bar{5}2$ $77\bar{8}$	−30 00	81 38	90 00	31 $02\frac{1}{2}$

Nevada crystals. It will be seen that four of the forms found on the Nevada crystals are new for this mineral.

A complete angle table for svanbergite is given in Table 3. The axial ratio used is that obtained on the Nevada crystals. Since strontium of svanbergite is in part replaced by calcium, the axial ratio varies dependent upon the Sr:Ca ratio.

On the basis of x-ray data (see following section) svanbergite could belong to any one of the three point groups, $3m$, 32 or $\bar{3}\ 2/m$. Hendricks[3] found alunite to be pyroelectric, although Gossner[4] made similar tests with negative results. Ygberg[5] made etch tests on svanbergite with negative results. Therefore, due to lack of evidence to the contrary, svanbergite has been placed in the centrosymmetrical point group $\bar{3}\ 2/m$.

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[3] Hendricks, S. B., The crystal structure of alunite and the jarosites: *Am. Mineral.*, **22,** 773–784 (1937).

STRUCTURAL DATA

Rotation, and zero-, first-, second and third-layer Weissenberg photographs, were taken about [0001] of a Nevada svanbergite crystal. These showed the space lattice type to be rhombohedral, and the Laue symmetry to be $\bar{3}\ 2/m(D_{3d})$. The possible space groups are $R\,3\,m$, $R\,32$, and $R\,\bar{3}\,m$. In his work on the structure of svanbergite, Pabst[6] adopted the space group $R\,\bar{3}\,m$. If svanbergite, like alunite, is pyroelectric, the correct space group would be $R\,3\,m$.[7]

TABLE 4. ANALYSIS OF SVANBERGITE FROM NEVADA

	1	2	
Al_2O_3	36.91	0.3621	$=3\times0.121$
Fe_2O_3	0.24	0.0015	
CaO	3.25	0.0580	$=2\times0.091$
SrO	12.84	0.1239	
P_2O_5	16.70	0.1176	$=1\times0.118$
SO_3	17.34	0.2166	$=2\times0.108$
H_2O	12.51	0.6942	$=6\times0.116$
	99.79		

1. Analysis by F. A. Gonyer.
2. Molecular ratios.

The unit cell dimensions[8] of Nevada svanbergite, obtained by measurements of rotation and zero-layer photographs about [0001], are as follows:

$$a_0 = 6.99 \pm .05\ \text{Å}$$
$$c_0 = 16.75 \pm .05\ \text{Å}.$$

These dimensions correspond to an axial ratio of $c:a=2.3963$.

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[4] Gossner, B., Über Sulfate und Phosphate mit ähnlichen Kristallgitter: *Zeit. Krist*, **96,** 488–492 (1937).

[5] *Op. cit.* p. 8.

[6] Op. cit.

[7] Hendricks, S. B., *Op. cit.*

[8] In the calculation of unit cell dimensions and density the following constants were used: $\lambda CuK\alpha=1.542$; $\rho=1.66020\ \Sigma A/V$.

CHEMISTRY

Svanbergite from Nevada was analyzed by Mr. F. A. Gonyer of the Department of Mineralogy, Harvard University. The analysis is very similar to those given for material from Westanå and Horrsjöberg, Sweden.

The analysis of Nevada svanbergite is given in Table 4. The unit cell contains $3[(Sr, Ca)Al_3(SO_4)(PO_4)(OH)_6]$. The calculated density, using the unit cell dimensions given in the preceding section, is 3.24, which compares favorably with the measured density of 3.22 ± 0.02.

OPTICAL PROPERTIES

Svanbergite from Nevada has the following optical properties:

$$\text{Uniaxial } (+). \quad \left.\begin{aligned} \omega &= 1.635 \\ \epsilon &= 1.649 \end{aligned}\right\} \pm 0.002.$$

SENGIERITE: A PRELIMINARY DESCRIPTION

J. F. VAES[1] AND PAUL F. KERR[2]

ABSTRACT

A hydrous copper, uranium, vanadium mineral from Katanga, Belgian Congo, with the formula $2CuO \cdot 2UO_3 \cdot V_2O_5 \cdot 10H_2O$, is believed to be a new mineral and is called sengierite in honor of Mr. Edgard Sengier. X-ray diffraction, chemical analysis, spectrographic study, crystallographic measurement, and optical study combine to suggest that the material described is related to carnotite and tyuyamunite, but differs chemically in that it is a definite copper-bearing species. In crystallization it may be quite similar to the other two minerals.

INTRODUCTION

An unusual radioactive mineral has been found in fissures cutting an argillaceous phase of the Mines Series, in the Elizabethville-Jadotville area of Katanga in the Belgian Congo. Chemical, *x*-ray and crystallographic data indicate that the mineral differs from species previously described. This particular portion of the Mines Series (pre-Cambrian) is described by geologists of the Union Miniere as R.A.T. (Roche Argilo-Talqueuse) and consists essentially of chlorite and talc. The mineral occurs in the form of small, green, platy crystals which correspond approximately to the empire green of Ridgway (1912), have a vitreous luster and coat fracture surfaces in a flake-like fashion as shown in Fig. 1.

The fissures containing the crystals occur along a fault which brings the R.A.T. into contact with a dolomite containing minor sulfide mineralization in the form of siegenite. The mineral is accompanied by black oxides containing iron, copper, cobalt, and nickel and also some lustrous yellow volborthite. Less frequently it is found associated with vandenbrandeite, fibrous malachite, garnierite, and chrysocolla. Pitchblende is also found in small pockets along the fault where it has been partly altered to vandebrandeite and kasolite. The mineral is believed to be of supergene origin produced by deposition from solutions containing uranium, vanadium, and copper derived from earlier minerals.

The name *sengierite* is proposed for the new mineral in honor of Mr. Edgard Sengier, Executive Director of the Societé Générale de Belgique and Managing Director of the Union Minière du Haut Katanga, in recognition of his efforts in directing war-time mineral production from the Belgian Congo. The Congo production of copper, tin, cobalt, industrial diamonds, and various minerals was much more of a material factor in Allied success than has been generally realized.

The locality which yields the mineral was first recognized by Dr. H. G.

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[1] Union Minière du Haut Katanga.

[2] Columbia University.

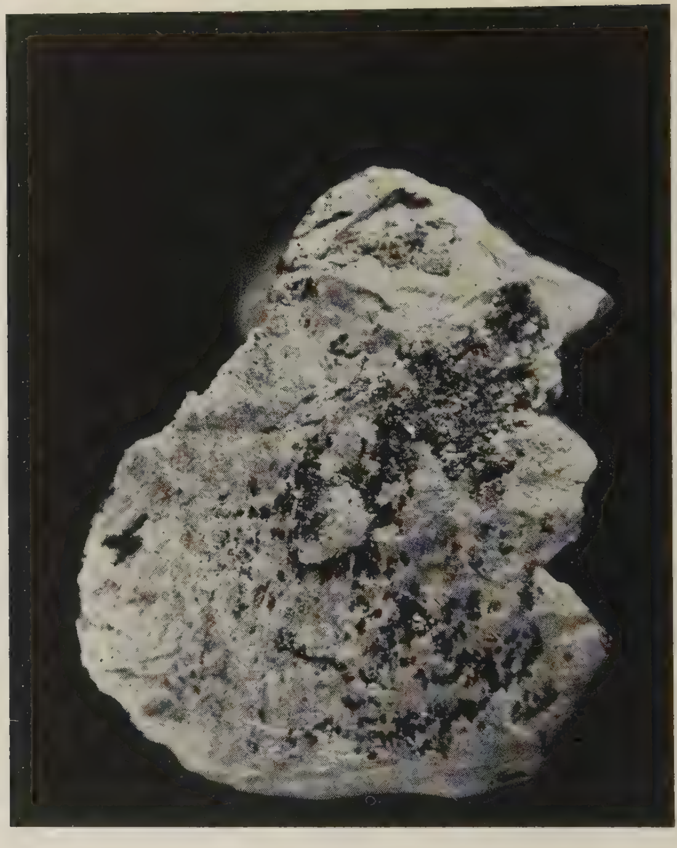

FIG. 1. Crystals of sengierite distributed on a surface of fractured rock (about one and one half times natural size).

Schuiling, Chief Geologist of the Union Minière and Dr. Anton Gray, Chief Geologist of the Kennecott Copper Corporation. The mineral itself was first identified by Mr. Vaes. Confirming studies have since been made at Columbia University on the basis of data and techniques not available at Jadotville. The laboratory work at the University has been carried on with the assistance of Mr. H. D. Holland. We are also indebted to Professor T. I. Taylor of the Department of Chemistry for cooperation in spectrographic studies. We likewise appreciate the courtesy of Dr. Michael Fleischer of the U. S. Geological Survey who read the manuscript on behalf of the Society and offered a number of constructive suggestions.

CRYSTALLIZATION

Sengierite is orthorhombic in crystallization and apparently belongs to the bipyramidal class. The crystals rarely measure as much as two

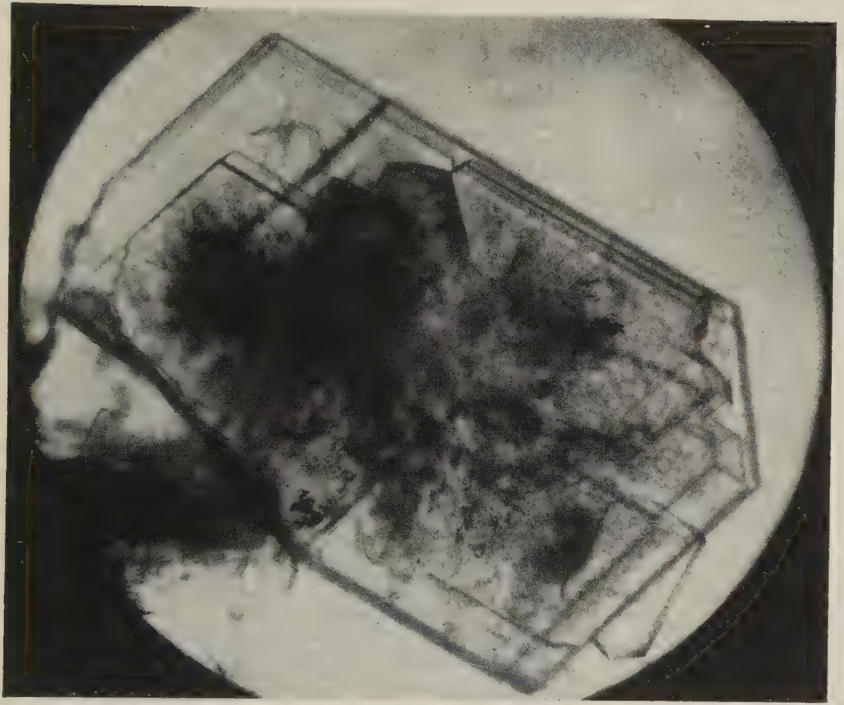

FIG. 2. Photomicrograph of a crystal of sengierite. Magnification about 50.

millimeters across and are ordinarily not more than a fraction of a millimeter in width. The habit is tabular with the thickness usually one-fifth to one-tenth the width. The outline is rhombic, the two opposite acute corners of the section often being truncated by a pinacoid. Crystals show excellent cleavage parallel to (001) and are frequently only singly terminated. The occasional occurrence of doubly terminated bipyramidal crystals leads to the conclusion that the mineral belongs to the bipyramidal class. Figure 2 shows such a doubly terminated crystal. Angles were measured with a two circle goniometer although imperfections in crystal development interfered with the attainment of as much precision as should be possible with such an instrument. Oscillatory development parallel to the basal plane introduces ray-like reflections with the goniometer for certain faces. On the basis of the unit face assumed, the axial ratio is $a:b:c=0.762:1:0.739$.

The forms most frequently observed are (001), (111) and (010). The rhombic prism (110) and dome (011) and the rhombic bipyramids (331) or (441) are often present.

In measuring the interfacial angles six different crystals were selected with a binocular microscope. Measurements of the rhombic prism (110) were repeated three times for each individual face, the average being recorded. Among the interfacial angles measured $(110)\wedge(1\bar{1}0)$ were repeated on 5 crystals; the angles $(\bar{1}10)\wedge(\bar{1}\bar{1}0)$ on three crystals; the angles $(1\bar{1}0)\wedge(\bar{1}\bar{1}0)$ on 5 crystals, all giving either good or fair measurements. The weighted average of all measurements yields the angle $(110)\wedge(1\bar{1}0)$ of 74° 37′ used to compute the $a:b$ ratio of $0.762\pm.001$.

The $b:c$ ratio has been determined on the basis of measurements between the pinacoid (001) and the rhombic bipyramid faces. The bipyramid faces tend to develop multiple reflections along the vertical circles, hence the measurements are less accurate than those of the rhombic section. The weighted average of measurements on six crystals is $(001)\wedge(111)=50°\ 40'$ which yields a $b:c$ ratio of $1:0.739\pm0.073$.

Although observed angles were not sufficiently well developed on the crystals available for measurement, it seems likely that the forms (331) and (441) are present. Although other bipyramidal forms may be observed, the angles were not considered sufficiently significant for purposes of record.

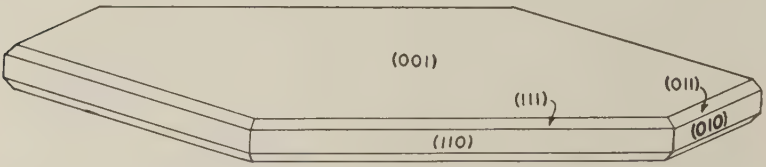

FIG. 3. Sengierite, showing the pinacoids (001) and (010), with the rhombic prism (110), dome (011) and the rhombic bipyramid (111).

OPTICAL PROPERTIES

The dispersion is $v<r$ and the pattern is symmetrical. The angle $2V$ on the basis of micrometer ocular readings is 37°–39°. Sengierite is biaxial, negative, and yields a good interference figure with strong dispersion. The acute bisectrix is perpendicular to (001) and the plane of the optic axes is parallel to (010). The indices of refraction were determined by the immersion method using melts as follows:

$$\alpha = 1.77; \qquad \beta = 1.94; \qquad \gamma = 1.97.$$

Interference colors are somewhat obscured by the natural color of the mineral. The pleochroism is distinct with $X=c=$bluish green; $Y=b$ $=$olive green; $Z=a=$yellowish green to colorless. A view of the crystals as observed with the microscope appears in Fig. 3.

Chemical Properties

An approximate chemical analysis of sengierite on 0.1460 grams of material was made by Mr. Bracq of the Jadotville-Panda Laboratory of the Union Minière as follows:

	Analysis	Recast	Theoretical Composition
CuO	14.82	15.77	14.55
V_2O_5	15.96	16.98	16.65
UO_3	47.45	50.47	52.34
$(Fe, Al)_2O_3$	1.43		
H_2O	15.77	16.78	16.46
	95.43	99.70	100.00

The above yields the formula $2CuO \cdot 2UO_3 \cdot V_2O_5 \cdot 10H_2O$. Unfortunately, samples with sufficient quantities of separable material to make possible the analytical precision desired do not appear to be available.

In order to obtain confirmation of the chemical nature of the mineral a spectrographic plate was secured showing the lines for sengierite in comparison with the lines of copper, vanadium, and uranium and referred to iron. A portion of this plate enlarged is shown in Fig. 4. It may be observed that each of the lines of sengierite may be matched by a corresponding line for either Cu, V, or U in the portion of the spectrographic plate reproduced. This same comparison would apply throughout the range from 3020 to 4400 Angstroms. In view of this comparison, the spectrographic data would indicate that the essential metallic elements of the sengierite are Cu, V, and U, in confirmation of the chemical determinations.

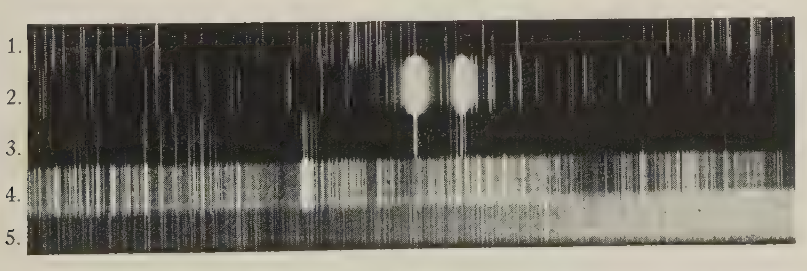

Fig. 4. Comparison of a spectrogram of sengierite with spectrograms of iron, copper, vanadium, and uranium between 3020 Å and 3475 Å.

1. Iron
2. Copper
3. Sengierite
4. Vanadium
5. Uranium

The water content of sengierite was determined on a sample weighing 0.080 gr. and containing 0.0090 gr. of gangue. The loss during heating was found to be as follows:

Temperature	Per cent Loss	Mol. H_2O
100° C.	3.94	2.5
300° C.	10.56	6.5
Calcination	15.77	10.

When heated at 300° C. and re-exposed to air for two days the mineral regained water, the loss being 6.48 per cent or 4 molecules H_2O. Thus, it seems likely that the mineral contains 10 molecules of H_2O, six of which are quite stable.

When heated in a closed tube, sengierite loses water, assumes a bronze shade with a metallic luster and becomes opaque. The mineral dissolves readily even in dilute hydrochloric acid. In concentrated acid a brown ring is formed around the grains of the mineral, indicative of the presence of vanadium. The solution gives a test for copper, and after repeated precipitations with ammonia, accompanied by dissolving the precipitate formed in hydrochloric acid, the solution yields enough uranium soluble in acetic acid to yield the microchemical reaction with sodium acetate. Tests for calcium, potassium, magnesium, and phosphate applied to solutions of sengierite have all been negative.

X-Ray Data

The *x*-ray diffraction pattern obtained for sengierite by radiation from copper through a nickel filter was compared with patterns obtained under similar conditions from samples of carnotite and tyuyamunite from the Egleston Collection of Columbia University. It was found that the patterns obtained from specimens of carnotite, Florence Mining Claim, Camp Marvel, Naturita, Colorado; of "carnotite" from the Copper Prince Mine, Rock Creek, Colorado; "tyuyamunite and carnotite" from Paradox Valley, Colorado; and tyuyamunite, Hudspeth County, Texas, could be arranged on the basis of line spacings to form a series in which carnotite and tyuyamunite are end members, and in which the other two specimens occupy intermediate positions. The pattern obtained from sengierite was similar to the patterns obtained from members of this carnotite-tyuyamunite series, but differed sufficiently from each of the four patterns to suggest its identity outside the series. Sengierite, with 2CuO in the position occupied by K_2O in the carnotite formula and structurally similar, is perhaps not a direct end-member of a carnotite-sengierite series but is presumably a cuprian mineral closely related to carnotite.

Table 1. Comparison of Interplanar Spacings of Sengierite, Tyuyamunite, and Carnotite

Sengierite, Katanga		Tyuyamunite, Hudspeth Co., Tex.		Carnotite, Naturita, Colo.		
d in Å	Est. Int.	*d* in Å	Est. Int.	*d* in Å	Est. Int.	
9.883	10	10.180	10	11.142	3	
6.566	1	6.620	3	6.425	10	
5.736	1	—		—		
4.915	10	5.019	9	5.063	3	
4.160	2	—		—		
4.020	3	4.021	2	—		
3.710	3	—		—		
—		3.366	3	3.493	6	
3.153	10	3.202	5	3.208	3	
—		3.123	3	3.092	8	
2.951	2	—		2.998	3	
2.836	2	—		2.822	1	
2.721	1	2.693	1	2.742	2	
2.549	3	—		2.552	3	Average error
2.433	3	2.484	1	2.452	2	= ±0.005 Å
—		—		2.356	$\frac{1}{2}$	Max. error
2.252	1	2.275	1	2.267	1	= ±0.015 Å
2.128	3	2.159	1	2.146	3	
2.086	3	2.096	1	2.081	2	
2.052	1	2.039	4	—		
2.001	4	—		2.016	2	
—		1.964	1	1.934	3	
		1.911	2	1.901	2	
1.857	3	1.870	1	1.864	1	
1.802	1	—		1.816	1	
1.760	3	—		1.756	1	
1.715	2	—		—		
1.667	1	—		1.670	2	
1.632	1	—		—		
1.588	1	—		1.599	2	
1.508	1	—		1.500	2	

Table 1 contains data on interplanar spacings for sengierite, carnotite, and tyuyamunite, calculated from the *x*-ray patterns.

Identity of Sengierite

In view of the large number of hydrous uranium minerals the review of the literature in connection with establishing the unique character of a new species is not as simple a procedure as might be desired. However, search of the ordinary journals and the various mineral listings fails to

TABLE 2. SUMMARY OF THE PROPERTIES OF THE HYDROUS URANIUM VANADIUM MINERALS

Properties	Sengierite	Carnotite	Tyuyamunite	Rauvite	Uvanite
Chemical formula	$2CuO \cdot 2UO_3 \cdot V_2O_5 \cdot 10H_2O$	$K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$	$CaO \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$	$CaO \cdot 2UO_3 \cdot 6V_2O_5 \cdot 20H_2O$	$2UO_3 \cdot 3V_2O_5 \cdot 15H_2O$
Calculated analyses	$CuO = 14.6$ $UO_3 = 52.3$ $V_2O_5 = 16.6$ $H_2O = 16.5$	$K_2O = 10.4$ $UO_3 = 63.5$ $V_2O_5 = 20.1$ $H_2O = 6.0$	$CaO = 6.4$ $UO_3 = 65.2$ $V_2O_5 = 20.7$ $H_2O = 7.7$	$CaO = 2.7$ $UO_3 = 27.5$ $V_2O_5 = 52.5$ $H_2O = 17.3$	$UO_3 = 41.2$ $V_2O_5 = 39.3$ $H_2O = 19.5$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	—	Orthorhombic?
$a:b:c$	0.762:1:0.739	0.81:1:–	1.303:1:2.337	—	—
Habit	Rhombic plates acute <74°37′	Rhombic plates acute <78°	Elongated plates $(110) \wedge (1\bar{1}0) = 75°$	Fine aggregates	Fine aggregates
Cleavage	(001) perfect	(001) perfect	(001) perfect (010) and (100) dist.	—	(two) pinacoids
Hardness, tenacity	2½—brittle	4—very brittle	brittle	very brittle	—
Sp. Gr.	±4	4.46	3.31–4.35	—	—
Luster	Vitreous to adamantine	—	Pearly (001); adamantine	—	—
color	empire green	yellow to greenish yel.	canary yellow	Purple red	brownish yellow
streak	light green	—	light yellow	light brown to yel.	—
Indices α	1.76 to 1.77	1.75 to 2.06	1.670 to 1.77		1.817
β	1.92 to 1.94	1.925 1.895 —	1.870 to 1.93	1.87 to 1.90	1.879
γ	1.94 to 1.97	1.95 1.92 2.08	1.895 to 1.97		2.057
	(Vaes) (Kerr)	(Larsen and Berman)	(Larsen and Berman)		
Orientation	X = c; bluish green to colorless	X = c; grayish yellow	X = c; almost colorless		X = light brown
	Y = b; olive green	Y = b; lemon yellow	Y = b; canary yellow		Y = dark brown
	Z = a; yellowish green	Z = a; lemon yellow	Z = a; darker yellow		Z = greenish yellow
Optic Angle 2V	37°–39°	39°–44° small	36° 40°–55°		52°
Sign	—	—	—		+
Plane	∥ (010)	∥ (010)	∥ (010)		—
BXa	⊥ (001)	⊥ (001)	⊥ (001)		—
Dispersion	$r<v$ strong	$r<v$ weak	$r<v$ rather strong		—

reveal the description of a mineral corresponding exactly to sengierite.

The hydrous copper-uranium minerals are zeunerite, uranospathite, slightly-copper-bearing tyuyamunite, torbernite and metatorbernite, cuprosklodowskite, vandenbrandeite, and uranochalcite. Of these, only the cuprian tyuyamunite also contains vanadium. The hydrous vanadium-uranium minerals uvanite, carnotite, rauvite, and "ferganite"* contain vanadium but not copper. The compositions of the other hydrous uranium minerals have only UO_3 and H_2O in common with that of sengierite.

Of the copper-uranium and vanadium-uranium minerals mentioned above, all except vandenbrandeite, uvanite, rauvite, carnotite, and tyuyamunite contain either arsenic, phosphorus, or sulfur, all of which have been shown to be essentially absent from sengierite. The chemical, optical, and crystallographical properties of the above-mentioned copper-uranium and vanadium-uranium minerals most closely approximating the properties of sengierite are listed in Table 2. It would appear as shown by the chart that carnotite and tyuyamunite are the minerals in this group which are most closely related to sengierite. This has been confirmed by the x-ray diffraction data mentioned above.

Carnotite was first described by Friedel and Cumenge in 1899 from a locality at Montrose, Colorado, as a distinct hydrous uranium vanadate, and reported to have the composition cited below. Shortly thereafter Hillebrand and Ransome (1900) analyzed material from the same locality but obtained a somewhat different composition. In 1910 Crook and Blake described carnotite from Olary, South Australia. The composition cited by these authors was quite similar to that of Hillebrand and Ransome, and is given below. Crook and Blake measured the angles of small rhombic crystals of carnotite and found that the acute angle of the rhombic section was 78°.

Hillebrand again published descriptions of carnotite in 1924. He had found that the water content of carnotite varies strongly with atmospheric conditions and adopted a standard drying procedure for all samples prior to analysis. His bulk analysis for selected carnotite from Temple Mountain, Utah, dried at 20° over sulfuric acid of specific gravity 1.05 is cited below. Hess and Foshag (1926) examined carnotite from Colorado. Their analyses agreed with the hypothetical formula $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 2/3H_2O$. Optical measurements gave the value $\alpha = 2.06$ $\gamma = 2.08$, $2V = 50°$. In a later description by the same authors (1927), these results were supplemented by further optical data and an analysis of air-dried material reproduced in Table 3.

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* Shown by Nenadkevitch (1912) to correspond to tyuyamunite as pointed out by Dr. Fleischer.

Table 3. Analyses of Carnotite Mentioned in the Text

	Friedel and Cumenge (1899)	Hillebrand and Ransome (1900)	Crook and Blake (1910)	Hillebrand, Hess and Foshag	
				(1924)	(1927)
UO_3	63.54	61.53	60.8	62.26	65.62
V_2O_5	20.12	20.72	21.4	20.57	21.12
K_2O	10.37	7.31	6.6	10.00	9.58
CaO		3.03	1.3	0.66	0.64
H_2O	5.95	(−105°) 2.72	5.0	4.90	1.35
		(+105°) 2.36			
P_2O_5		0.90	trace		trace
BaO(SrO)		1.03			
MgO		0.25	trace	0.30	0.22
Na_2O		0.15	2.3	0.16	0.35
PbO			1.7		
CuO				0.07	
SO_3				0.26	
Fe_2O_3				0.55	0.04
Al_2O_3					0.10
Insol.				0.04	0.32
	99.98	100.00	99.1	99.77	99.40

Table 4. Analyses of Tyuyamunite

	Nenadkevitch (1912)	Hillebrand (1924) (Fergana)	Hess (1924)	Rode (1925)
UO_3	63.09	55.85	55.22	56.07
V_2O_5	21.	17.92	17.62	18.92
K_2O		0.17	0.47	
CaO	5.99	4.80	5.36	5.08
H_2O	7.04	16.61	14.79	17.53
BaO			0.26	0.32
MgO		0.09		0.12
Na_2O		0.20		
CuO		0.10		
Fe_2O_3		0.13	1.10	0.86
Tl	trace	trace		
Insol.		3.26	8.51	0.31
	97.12	99.13	100.33	98.71

From these analyses it appears that the formula $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$ where n is a function of the relative humidity and temperature of the surroundings, adequately describes the composition of carnotite. Copper is present only in small amounts. Confusion with sengierite is therefore hardly possible. This is supported further by the meager crystallographic evidence on carnotite which is available.

Tyuyamunite, first described in 1912 by Nenadkevitch, is a hydrous calcium-vanadium-uranium mineral. Some analyses of this mineral are given in Table 4. From these and other analyses the formula was deduced to be $CaO \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$, where n, as in the case of carnotite, depends somewhat on the humidity and temperature of the surroundings. Tyuyamunite has been considered a calcium analogue of carnotite. However, since n is usually much larger than in carnotite, some doubt has been expressed as to the isomorphism of these two minerals.

Crystallographic descriptions of tyuyamunite are to be found, among others, in articles by Hillebrand (1924), Hess (1924), and Dolivo-Dobrovosky (1925). The first of these authors cites Dr. H. E. Merwin who examined scales of tyuyamunite on two specimens supposedly from Paradox Valley, Colorado. He found that the scales were probably orthorhombic and tabular parallel to *c*(001). The forms present at the boundaries were *a*(100), *b*(010), *m*(110), and *l*(120). The prism angles *mm* were 75° and $105° \pm 1°$, and the prism (*ll*) 67° and $113° \pm 1°$. The crystals were found to be biaxial and negative; the acute bisectrix emerges normal to the plates, and the plane of the optic axes is parallel to *b*(010). It was found that $2E = 100°–115°$ and $2V = 45°–51°$. The refractive indices measured by immersion under the microscope, are $\gamma = 1.965–1.968$; $\beta = 1.927–1.932$, and $\alpha =$ (calculated) 1.75–1.80. On another specimen it was found that $\gamma = 1.92$, $\beta = 1.895$, α(caluclated) $= 1.78$.

Hess (1924) confirms this data. His measurement of $2V = 48°$, $\alpha = 1.72$, $\beta = 1.868$(?) and $\gamma = 1.953$ agree only approximately with Dolivo-Dobrovosky's values of $2V = 48°$, $\gamma - \beta = 0.028$, $\gamma - \alpha = 0.154$. The latter author gives the axial ratio as 1.303 : 1 : 2.337 on the basis of goniometer measurements of minute platy crystals from Tyuya Muyun. The angles measured were $(001):(110) = 52\frac{1}{2}°$, $(001):(111) = 70\frac{3}{4}°$.

As in the case of carnotite, it is probable that tyuyamunite is related to, but perhaps not identical in crystallization, with sengierite. The grouping of the three minerals together, however, seems justifiable with the potassium, calcium, and copper-bearing members being represented respectively by carnotite, tyuyamunite, and sengierite. While the crystallographic similarity is perhaps not as close as between the long-familiar autunite and torbernite in the uranite group, the justification for distinctive nomenclature is comparable.

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NOTES AND NEWS

GRAIN-THIN SECTIONS AND OTHER TEACHING AIDS IN OPTICAL MINERALOGY

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In an effort to make it possible for a student in optical mineralogy to study all of the optical characteristics of a mineral in a thin section, a method has been developed for making thin sections containing an ample number of grains of the same mineral in random orientations, in which each individual grain is completely surrounded by Canada balsam. The materials commonly used in the optical mineralogy laboratory for studying the optical properties of one particular mineral usually consist of:

(1) mineral grains or powder between 150 and 200 mesh for the immersion method,
(2) slides containing these grains, mounted in Canada balsam,
(3) a set of thin sections of a large piece of mineral at random orientation, usually showing only one orientation,
(4) thin sections of rock, containing among other minerals some grains of the mineral under consideration, and
(5) oriented slides containing one small piece of mineral at one special orientation.

The importance of the immersion technique is generally recognized and should be mastered by all serious students of rocks, minerals, and ores; nevertheless, it does not enable the student to observe all of the optical properties without going to considerable trouble if the mineral grains have a tendency to lie in a preferred orientation due to cleavage. As reference material in connection with thin-section work the use of grains is limited. Grains mounted in Canada balsam are of value for the transition from the immersion technique to thin-section work and acquaint the student with the relief of the particular mineral. Thin sections of one large piece of mineral at random orientation are of doubtful value, since the one orientation shown is seldom sufficient for the determination of the mineral, and if the appearance of the mineral under consideration in this one orientation becomes fixed in the mind of the student it is even misleading. As reference material a set of these slides is useless. Thin sections of rock containing the mineral have the advantage of showing the particular mineral among associated minerals, but in studying the optical properties the student spends much time in locating the few grains of the mineral in question present in the section, sees the mineral mostly in contact with other minerals, and as in the case of schists and gneisses, the mineral will occur only in one preferred orientation. The oriented slides are intended mainly for studying interference figures and are seldom of correct thickness. To be of real value these slides should be properly labelled, show some indication of the crystal orientation, and be of correct thickness. The ideal thin section for showing what the three last mentioned slides are intended to show would consist of a thin section containing around 200 grains of a certain mineral at random orientation, mounted in Canada balsam, and showing the crystal outline or orientation. The grains should be closely spaced to make comparison between grains of different orientation easy and impressive. All grains should be of correct thickness and large enough to give clear interference figures. The new slide reaches this ideal in some cases, but falls short in the following respects: (1) Only minerals which are not affected by salt water, and which break up in nearly equidimensional grains can be prepared by the new method. For this reason sections of gypsum, most micas, and fibrous minerals cannot be prepared. (2) In crushed material the crystal orientation can be determined only when the mineral has cleavage. It is seldom possible to obtain a large enough number of individual, well developed, small crystals between 9 and 60 mesh in size to make a slide. Another disadvantage of crushing the mineral is that since the twinning plane is often a plane of weakness, much twinning is eliminated in crushing. (3) The strength of the mineral to resist the grinding action varies with orientation and therefore, although the mineral grains are at random orientation in the blank grains in certain orientations are liable to be plucked out in the grinding operation. For this reason basal sections of amphibole and pyroxene are rather rare in a slide. (4) It is difficult to obtain mineral material which is absolutely pure. If the impurities occur as separate grains and in negligible amounts, these foreign grains can easily be removed from the slide before covering. On the other hand, if these impurities occur as inclusions, not much can be done about it. However, in general, one can say that as long as these impurities are characteristic associated minerals and do not occur in such quantities as to obscure the mineral under consideration, little harm is done by their presence.

Method of Preparation

In order to prepare thin sections of more than one particle on one slide, the individual pieces have to be mounted in some material which will permit the preparation of one common plane surface, and hold this surface at the elevated temperature of the hot plate while cementing to the glass slide. Secondly, since the abrasive action is severe on the edges of hard particles imbedded in a soft matrix, a cement stronger than Canada balsam should be used.

For a mounting medium thermosetting plastics have the disadvantage that the plastic cannot easily be removed after the section is prepared and the index of refraction of the transparent varieties does not match the index of Canada balsam. Thermoplastic plastics neither match the index of Canada balsam nor hold a sufficiently plane surface on the hotplate. Although lucite has been used for making sections of pebbles, it has been found less advantageous in grinding properties and more difficult to use than plaster of Paris. In the preparation of grain-thin sections, plaster of Paris is used. The crushed and sieved grains—best results are obtained with grains between 9 and 60 mesh—are mixed dry with plaster, then water is added until a creamy paste is formed and the mixture poured into a mould 22×22 mm. and $\frac{1}{4}''$ deep. Since the consistency of the mixture is of utmost importance, particularly the amount of water, the exact measurements for quartz (and most other minerals) are here given for 6 blanks of the above given size: 12 cc. dry washed grains, 20 cc. plaster, and 7.5 cc. ±.2 cc. water. With some minerals the amount of water may be slightly different. The mineral grains inside the blank are at truly random orientation. If a preferred orientation is desired the moist grains can be arranged on a glass plate and the plaster poured over it.

After the blanks are set, thin sections of them are prepared in the usual manner except that instead of Canada balsam, Lakeside No. 70 transparent cement is used.* The finished thin section contains the grains in a matrix of plaster of Paris. Plaster is soluble in small amounts in water, but to dissolve the thin layer present required up to 48 hours. Adding salt (NaCl) to the water speeds the process to 1 or 2 hours. As soon as all plaster is dissolved, the scum left on the slide is washed off in water and any dirt caused by grinding is cleaned off with xylene. The sections are then covered in the usual manner, using a slightly larger amount of balsam to fill the space between grains.

ADDITIONAL SPECIAL SLIDES

In addition to grain-thin sections, four additional slides have been made for the purpose of studying interference figures and relief. The idea behind these slides was that it is an advantage to see objects for comparison with each other, either simultaneously or in quick succession. For this reason a relief scale was made containing 6 grains of the following minerals: fluorite, orthoclase, quartz, beryl, apatite, and garnet, mounted in the form of a star. The grains are sufficiently close together to make it possible to bring the center of the star with all six minerals simultaneously into the field of the 16 mm. objective. The star is located in a hole of a thin paper mask bearing the names of the minerals. This makes it easy to find the mount on the slide. For interference figures a slide with a mask with 6 holes is used. Each hole contains an oriented plate of mineral and the different interference figures can be brought into view by sliding the section from hole to hole without refocusing. The slide contains the following orientations: quartz, perpendicular to c for uniaxial positive; topaz, perpendicular to Bx_a positive; muscovite, perpendicular to Bx_a negative; epidote, optic axis; barite, perpendicular to Bx_o; and topaz cut halfway between optic axis and Bx_a so that one emergence point and the center of the Bx_a are simultaneously in the field. This orientation demonstrates the mechanism of the isogyres in a spectacular manner. All plates are cut to a thickness to show the interference figures to best advantage and selected minerals of extreme clearness are used for the purpose.

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* Properties of Lakeside #70 cement are discussed under the heading "Notes on Lakeside #70 Transparent Cement" by the author.

To enable the student to get acquainted with the appearance of the isogyres for different values of 2V, a similar slide has been prepared containing plates perpendicular to the Bx_a of the following minerals: phlogopite 7.5°, aragonite 18°, muscovite 40°, topaz 60°, orthoclase 70°, andalusite 84^c. Since the optic axis angle of most of these minerals is variable, a simple device for measuring the optic axis angle was constructed with which the angle can be determined to $\pm 1°$ directly from the interference figure. This device consists of a $\frac{3}{8}'' \times 1'' \times 2''$ brass plate to which are attached sheet-brass legs by which it can be held on the stage of the microscope by the stage clips, and a protractor which is fastened to one $\frac{3}{8}'' \times 2''$ side. Through the center of the protractor half-circle, a $\frac{1}{8}''$ hole is drilled, which is extended through the width of the plate. A shaft which passes through this hole carries on the protractor side an arm with a pointer; on the other side a thin plate 32 GA$\times \frac{3}{8}'' \times \frac{1}{2}''$ which has a $\frac{1}{4}''$ diameter hole in the center. A friction spring holds the shaft in any desired position. From the mineral crystal a plate is cut approximately perpendicular to the Bx_a and mounted on an 8 mm. square cover glass. One-fourth inch diameter glass hemispheres are cemented to the cover glass and over the mineral plate in such a way as to form a complete sphere. These hemispheres are made by melting the end of a glass rod, sawing off the rounded end, and grinding the flat side to form a hemisphere. With a small blocking tool for grinding, these hemispheres can be made quickly and the curvature is sufficiently accurate for giving a sharp image when the hemisphere is used as a lens. The mounted mineral plate is now inserted into the $\frac{1}{4}''$ hole in the metal plate, the interference figure is obtained with the medium power objective without throw-out condenser and with the substage at its highest position. The cover glass is turned until the optic plane is parallel to the plane of the protractor. Then the stage of the microscope is set to the 45° position, and the protractor arm turned until the emergence point of one optic axis is lined up with the cross-hair. After the angle has been read, the arm is turned until the other emergence point is in line. The angle between the two measurements is 2E of the mineral against the index of the hemispheres. When the index of the glass of the hemispheres is known, the angle 2V can be computed. This device can easily be made and can be used in class for giving a vivid demonstration to clarify the relation of the optic axis figure to the Bx_a.

Since most beginning students have difficulty in distinguishing the Bx_a from the Bx_o for large optic axis angles, a fourth special slide is provided, with two holes in the paper mask. In one hole a plate of andalusite 84° Bx_a is mounted, while the other hole has a plate of the same mineral cut for Bx_o. With this slide the student can observe quickly the difference in appearance between the two figures.

It is believed that a set of these mineral slides in connection with the monomineralic grain-thin section will eliminate much waste of time in the laboratory and give the student a vivid and complete conception of the optical properties of the different minerals. The same set could be used to advantage as a reference set in further studies in petrography.†

Grain-thin sections have been used for the following purposes other than teaching aids: (1) in sedimentary problems for the identification of mineral grains in fractions coarser than 100 mesh; (2) for control of non-metallic coarse concentrates in the concentrating process; (3) for examination of churn drill sludge.

ACKNOWLEDGMENTS

The author expresses thanks for their kind help and interest to: Dr. Ian Campbell of the California Institute of Technology for encouraging the development of these slides in the thin-section laboratory, for his valuable suggestions and interest in the work, and criticism while the work was in progress; to Dr. George Tunell for contributing helpful suggestions and much encouragement, and for reading the manuscript; to Dr. R. H. Jahns, who contributed the suggestion for the Bx_a-Bx_o slide and a supply of 40° muscovite with constant optic axis angle in the different cleavage lamellae; to Dr. Clay T. Smith, who suggested the optic axis angle slide and showed much interest in the progress of the work; to Dr. Wyatt Durham, who recommended the use of salt water for dissolving gypsum.

California Institute of Technology
Division of Geological Sciences
Contribution No. 465

NOTES ON LAKESIDE NO. 70 TRANSPARENT CEMENT

RUDOLF VON HUENE, *California Institute of Technology.*

Since Lakeside No. 70 cement is rapidly taking the place of Canada balsam as a mounting cement for preparation of thin sections, a few words in regard to its properties and use seem appropriate. Meyer* mentions the following properties: index 1.54, insoluble in petroleum, melting temperature 140°, easy to apply and grind, more viscous than Canada balsam and therefore prevents spreading of the section in covering. The index of refraction of a cement used for the preparation of thin sections is of utmost importance, and since any cement which is not reasonably stable in this respect would be useless, a study of the ageing quality of this cement was undertaken before it was used for ordinary thin sections. The first batch of this cement was obtained by the author in January, 1944, and was used only for sections which had to be ground in oil. It was widely recommended by the author for this purpose for its superior strength, insolubility in mineral oils, and good grinding properties. The index was not measured at this time, but slides were prepared in which the index of the cement could be compared with that of orthoclase and quartz. By April, 1947, no ill effects of ageing could be observed in the slides and prisms were prepared from the 1944 batch of cement, and a new batch just received. The index of both prisms was measured as 1.5369 for sodium light. After this it was felt that the cement was sufficiently uniform and stable for general use, and has been used since for mounting all slides. The cement is somewhat liable to cause bubbles at temperatures above 150° and is too viscous below 140°, and therefore requires somewhat closer control of the hot-plate temperature than does Canada balsam. Its superior holding power and resistance to bruising make it an ideal mounting medium. At first it seemed unsuitable for impregnation due to surface tension, but later it was found that when the surface of the chips was moistened with kerosene before applying the cement, the surface tension was reduced and the cement flowed sufficiently deep into the rock to permit grinding of a flat surface. For covering, Canada balsam is still preferred, particularly for the reasons mentioned by Meyer. The 1944 prism was stored for one year at an elevated temperature over the hot plate and the measurement repeated, giving an index of 1.5366. The measurement was made on a Gaertner one-circle goniometer to within ±.0002. Therefore the lower index after ageing does not necessarily indicate that the index has a tendency to get lower with time. At the same time two other batches of Lakeside No. 70 were measured; one of darker color than usual showed an index of 1.5371, and one of the usual color showed 1.5358 for sodium light. The dispersion of Lakeside No. 70, cooked Canada balsam, and the ordinary ray of quartz is shown in Fig. 1 and Table 1. The index of Lakeside No. 70 is lower than the ordinary ray of quartz over practically the entire visible spectrum. For the measurements a helium tube as suggested by J. Glass† was used. The data for quartz were obtained from Hardy and Perrin "The Principles of Optics."

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† Sets of 40 mineral grain-thin sections and the four special slides are obtainable through Ward's Natural Science Establishment, Rochester, N. Y., or through the author.

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* Notes on cutting and polishing of thin sections: *Ec. Geology*, **41**, 166–172 (1946).

TABLE 1

Wave Length	Canada Balsam	Lakeside No. 70
4713	1.5573	1.5495
5016	1.5502	1.5432
5890	1.5417	1.5358
6678	1.5382	1.5319

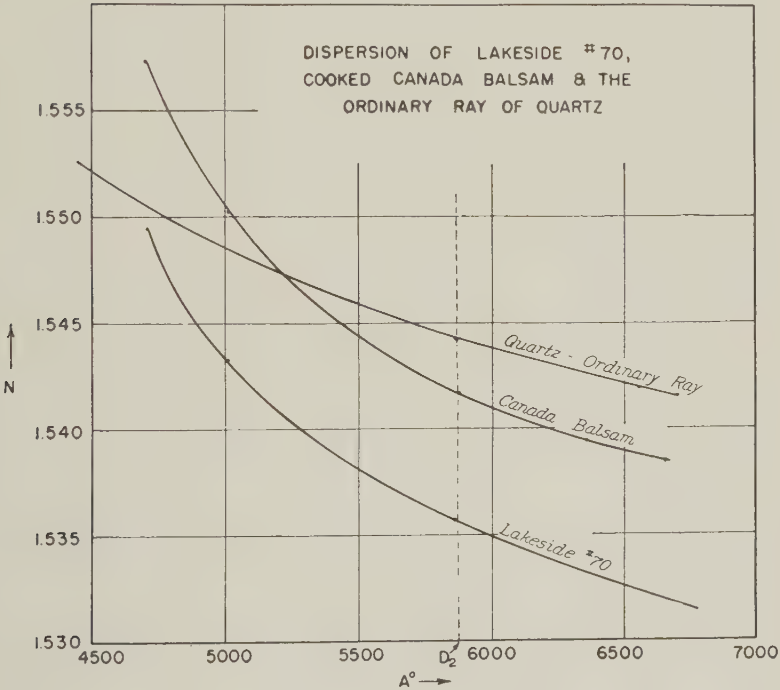

FIG. 1

The author expresses his thanks to Dr. George Tunell for encouraging the publication of these observations and for reading the paper.

California Institute of Technology
Division of Geological Sciences
Contribution No. **466**

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† Glass, J. J., Standardization of index liquids: *Am. Mineral.*, **19**, 459–465 (1934).

BOOK REVIEWS

GESTEINE UND MINERALLAGERSTÄTTEN. Vol. I, Allgemeine Lehre von den Gesteinen und Minerallagerstätten, by PAUL NIGGLI, with special assistance on Part IV by ERNST NIGGLI.

This prodigious effort in the field of geological monographs is but the initial work of a three volume series which is rapidly nearing completion. The manuscript for Volume II, "Die exogenen Gesteine und Minerallagerstätten", is already complete, and Volume III, "Die endogenen Gesteine und Minerallagerstätten", is now in preparation. The book is published by the Verlag Birkhäuser of Basel, Switzerland, as number 3 of their "Textbooks and Monographs in the Provinces of the Exact Sciences, Mineralogical-Geotechnical Series." Bound copies sell for 46 Swiss francs.

The fundamental concept of Volume I is expressed by Professor Niggli in the introduction where he states (in translation), "The majority of similar works are subdivided at a very early stage into sediments, igneous rocks, and metamorphic rocks; the exposition of the fundamental principles commands only very little space. Since, in the opinion of the author, this early splitting of and development of separate concepts as well as a frequently encountered lack of preliminary information about the associated sciences have worked out unfavorably, an attempt at a new type of presentation had to be undertaken." Indeed, the presentation is unorthodox for a book that purports to consider rocks and mineral deposits.

The work describes neither rocks nor mineral deposits, but concerns itself with constructing a framework of pertinent principles in geochemistry, crystal chemistry, physical chemistry, and geophysics. Part I, which deals with the material foundation, i.e., the nature of the constituents, considers the general chemistry of rocks, and the geochemical rules that govern the distribution of elements in the earth. This leads to a discussion of the formation of radicals and molecules and the nature of the crystalline state. About 30 pages is devoted to a brief description of "the most important minerals." Formulae of the silicate minerals are expressed so that the coordination relationships of the atoms can be read. Thus the formula for albite, $[(\mathrm{SiO}_4/_2)_3(\mathrm{AlO}_4/_2)]\mathrm{Na}$, indicates a structure in which two tetrahedra connect at each corner of a silicate tetrahedron (i.e., one doubly-coordinated O atom occurs with three doubly coordinated O atoms), in which one-fourth of the Si positions are occupied by Al, and in which Na represents the cation element occupying the relatively large spaces between the tetrahedra. This scheme of representation will no doubt confuse those geologists who are not readily conversant with crystallographic notation.

Part II considers the spatial relationships between the constituents of rocks and mineral deposits, i.e., textures and structures. Space is also devoted to a discussion of the application of statistics to petrologic problems and to a section on methods of determining and representing the quantitative mineralogical composition of rocks. Grain sizes, grain shapes, inter-growths, overgrowths, aggregate forms, orientation, porosity, and permeability—all are treated from a fundamental viewpoint so as to provide a basis for interpretation of all types of mineral aggregates.

In Part III Professor Niggli is concerned with the physical chemistry of mineral deposits and of their formation. Subdivisions here include a treatment of the laws governing the stability and coexistence of minerals in combination, under which heterogeneity, equilibrium, the phase rule, and poly-component systems are discussed, and a section dealing with significant processes in the formation of minerals.

Ernst Niggli, in Part IV, develops fundamental geophysical concepts of the earth. Also, data are listed on temperature, pressure, viscosity, and elasticity. A section on applied geophysics describes methods for the delineation of geological structures and the discovery of mineral deposits, including gravimetric, seismic, electrical, electromagnetic, magnetic, radioactive, geothermal, and geochemical methods.

The final part deals with the fundamentals of classification of rocks and mineral deposits. The processes of mineral formation are listed as twofold: (1) those that function in the border zones of the lithosphere, atmosphere, and hydrosphere, and (2) those that are completed within the lithosphere. Rocks and mineral deposits resulting from the first set of processes are termed exogenic; those owing their origin to the second group are called endogenic. Under the first are included (1) the autochthonous rocks and deposits formed by weathering and (2) the sediments. The subdivisions of sediments are (a) clastic sedimentary rocks, (b) pelites, gelites, humites, and related rocks, (c) carbonate rocks, (d) sulfate, and chloride rocks, etc., and (e) snow and ice. The endogenic rocks are no longer first classified under the primary headings of magmatic and metamorphic but according to the intensity conditions of their formation. Niggli recognizes three intensity zones: the katathermal zone whose upper temperature limit is that of crystallizing igneous rocks, the epithermal zone whose lower temperature limits approach those normally prevailing on the surface of the earth, and the zone intermediate between these two, or mesothermal.

These three are grouped into two general divisions, (1) katathermal rocks and mineral deposits and (2) epi- to mesothermal rocks and mineral deposits. Group one includes most of the igneous rocks, including pegmatites, high temperature vein materials, as well as ortho- and paragneisses, and migmatites and (kata)diabrochites (rocks resulting from strong high-temperature hydrothermal and pneumatolytic alteration). In group two are placed the bulk of the metamorphic rocks (schists, quartzites, marbles, tactites, etc.) and low-temperature vein materials. The volume concludes with a valuable list of pertinent books and a very good index.

Without doubt this work represents one of the most significant contributions to mineralogy that has ever been published. In a brief review it is impossible to present adequately the tremendous scope of the book and to sample the wealth of detailed information that it pours forth in its 540 pages, 335 uniformly excellent illustrations, and 43 concentrated tables. The greatest value of the work is that it presents on a unified basis the fundamental principles and concepts ordinarily scattered through books on crystallography, crystal chemistry, mineralogy, petrology, petrography, metamorphism, geophysics, and economic geology. It is, in fact, a monograph on paragenetic mineralogy which considers the formation of rocks and mineral deposits from the threefold viewpoint of composition, spatial relationships, and genesis. In the minds of the average beginning or intermediate students it will probably result in much mental indigestion; but it will prove rich fare for advanced mineralogical and geological personnel.

E. Wm. Heinrich, *University of Michigan*

FOURIER TRANSFORMS AND STRUCTURE FACTORS. By Dorothy Wrinch. Asxred Monograph Number 2, (1946).

The science of x-ray crystallography depends upon the fact that matter scatters x-rays in a manner dependent upon the arrangement of extra-nuclear electrons in the scatterer. Given any arrangement of scattering matter, and the wave-length, incident direction and intensity of an x-ray beam, it is possible to calculate in a straight-forward manner the electric vector and the intensity of scattered radiation at any point in space surrounding the scatterer. The aim of structure analysis is to solve the converse problem: given the intensity of scattered x-rays in a region surrounding a scattering body, and given the incident beam direction, wave-length, and perhaps the incident intensity, what is the distribution of electrons responsible for the pattern of scattered radiation?

It is well known that this question is not answerable in a general way, since one can observe only the amplitudes of the scattered electric vectors but *not* their phases. Nevertheless, auxiliary information of a chemical or physical nature is sometimes available which permits deduction of the required phases; or these may be established by trial-and-error methods.

The relationship between the density of scattering material, expressed as a function of position, and the scattered electric vectors—also expressed as a function of position in surrounding space (this latter function being called the structure factor), can be presented in a manner which brings out the functional interdependence very beautifully and which facilitates mathematical transformation from one to the other in such a way as to give great insight into the influence of one function upon the other. Specifically, by proper choice of coordinate systems these two functions become the Fourier transforms of one another.

It is with some aspects of this relationship of the density-function and structure-factor as Fourier mates that the little volume by Dr. Dorothy Wrinch, *Fourier Transforms and Structure Factors*, is concerned. This work is the second in a series of monographs published under the auspices of the American Society for X-Ray and Electron Diffraction.

The purposes of Dr. Wrinch's work, as stated in her Preface, are: firstly, the study of the structure factors of certain atomic groupings of frequent occurrence in both inorganic and organic crystals; and secondly, an introduction to "the language of structure factors" as "a necessary preliminary to the interpretation of the intensity maps of crystals made up of megamolecules of unknown structure." Of the second aim, nothing more is said anywhere in the volume. In chapter 1 the Fourier transform relationships between a density function and its structure factor are outlined. Chapter 2 discusses the general influence of the positions and symmetry of distributions upon the nature of their transforms. These are expansions of concepts of Hettich,[1] Patterson,[2] Ewald[3] and others, to whom the Fourier transform viewpoint is originally due. Both of these chapters are of prime importance.

The remaining sections of the monograph are concerned with transforms of specific distributions. Chapters 3, 4 and 5 deal with transforms of sets of points, computations being carried out for equi-weighted points at the vertices of cubes, tetrahedra, and octahedra, in trigonal and hexagonal meshes, and within surfaces and volumes of certain figures. Chapter 6 is an extension of the preceding material to certain continuous distributions. Chapter 7 is a discussion of some effects of crystal shape and size.

The monograph contains much excellent material, succinctly written. It is a contribution to the theory of x-ray scattering which should be read by every investigator seeking for a fuller understanding of the relations between density distributions and scattering patterns. Nevertheless, the work leaves much to be desired. The full strength of the transform method is obscured when so large a part of a discussion of it is devoted to computations of transforms of special equi-weighted point sets. In this first extended discussion of the viewpoint it is disappointing to find so little background material in x-ray scattering and such absence of comparison between the Fourier integral treatment and the more commonly used analytical methods. There is a dearth of discussion of the contributions of previous investigators of the transform methods, and no reference is made to some of the most important earlier papers—among these, for example, the short but important review by Ewald[3] which appeared six years previously. The effects of space-group symmetry in the development of the transform of an entire unit cell from the transform of the "asymmetric motif" of the cell, as touched upon by Hettich[1] or Knott,[4] are not discussed in the monograph, although they are straightforward and among the most important applications of theorems concerning the influences of rotations and translations of a function upon its transform. No use of—and indeed no reference to—convolution theorems is made in the monograph, despite the elegance which these lend to the mathematical theory, and the deeper insight which they provide into its application in x-ray scattering problems. No discussion appears of such matters of practical importance as the relations between the *transform of a given function* and the *transform of that function sampled periodically with varying degrees of fineness.*

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[1] Hettich, A., Beitrage zur Methodik der Strukturbestimmung: *Zeit. Krist.*, **90**, 483 (1935).

[2] Patterson, A. L., The diffraction of x-rays by small crystalline particles: *Phys. Rev.*, **56**, 972 (1939). See also earlier papers.

[3] Ewald, P. P., X-ray diffraction by finite and imperfect crystal lattices: *Proc. Phys. Soc.*, **52**, 167 (1940).

Despite the incompleteness of her monograph—and it must be recognized that we are warned of some of these in her Preface—structural crystallographers owe Dr. Wrinch a debt of gratitude for focussing their attention once again upon Fourier transform methods. Those who have not read her volume owe it to themselves to do so.

R. Pepinsky, *Alabama Polytechnic Institute, Auburn, Alabama*

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[4] Knott, G., Molecular structure factors and, their application to the solution of the structures of complex organic crystals: *Proc. Phys. Soc. Lond.*, **52,** 229 (1940).

MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held on Thursday, October 7th, 1948, in the apartments of the Geological Society of London, Burlington House, Piccadilly, W.1 (by kind permission). The following papers were presented:

(1) On the Occurrence of Anatase in Sedimentary Kaolin

By Dr. G. Nagelschmidt, Mr. H. F. Donnelly, and Mr. A. J. Morcom.

The occurrence of anatase in sedimentary kaolins from Georgia, U.S.A., is described on the basis of chemical, x-ray diffraction and electron microscope studies. The anatase is of a size comparable to kaolinite which forms the chief constituent of the clays, but there is a slight tendency for it to be concentrated in the smallest size classes.

(2) A List of Catalogues of Meteorite Collections

By Dr. L. J. Spencer

A skeleton working list, compiled some years ago, has been found useful. Now that a Commission on Meteorites has been set up by the International Geological Congress, the list has been extended and it is offered for publication.

(3) Clinozoisite From Camaderry Mountain, Glendalough, Co. Wicklow

By Mr. R. W. Johnston (communicated by Prof. C. E. Tilley).

The clinozoisite is found with albite as veins within the amphibolite of Camaderry Mountain.

The zoned crystals display a range of optical properties which have been recorded before from other localites, but which are not usually associated with clinozoisite. The crushed material was separated into two fractions which represent the inner and outer portions of the zoned crystals. These two fractions have been investigated chemically and optically. The results, illustrated by diagrams, are compared with similar occurrences from the literature.

(4) An Optical and X-ray Examination of the Basic Slag Mineral, Silicocarnotite

By Dr. D. P. Riley and Mr. E. R. Segnit.

Blue pleochroic crystals of siliocarnotite from several sources were examined optically and by x-ray methods and shown to be orthorhombic $a=10.1$, $b=6.7$, $c=15.4$ Å, space group probably *Pnnn*, optics $\alpha\|b$, $\beta\|a$, $\gamma\|c$. The axial ratios $a:b:c=1.51:1:2.30$ agree with those determined goniometrically by Miers, 1.5023:1:2.2943. The crystals exhibit a considerable variety of habit, the most common habits being prismatic, plates (001), and blades (101) elongated along [010].

(5) Two Olivines From South African Melilite-Basalts

By Dr. Morna Mathias.

Two olivines from the Spiegel River and Klaasvoogds melilite-basalts of the Cape Province are analysed. Optical properties for the olivines are given. These show excellent agreement with the chemical results. The olivines belong to the forsterite-fayalite series, and do not contain significant amounts of Ca_2SiO_4. The presence of nepheline, leucite, analcime, apatite, and zircon in the Klaasvoogds melilite-basalt is described for the first time.

NEW MINERAL NAMES

Parajamesonite

Viktor Zsivny and Istvan v. Naray-Szabo, Parajamesonit, ein neues Mineral von Kisbanya: *Schweiz. mineralog. u. petrog. Mitt.*, **27,** 183–189 (1947).

Columnar crystals, with imperfect, rounded faces and without good terminations, are found up to 8×2 mm. in size. They may be orthorhombic, or of a lower symmetry. No cleavage was observed. Color gray. Sp. gr. 5.479, 5.485. Analyses gave: Pb 39.81, Fe 2.98, Sb 34.74, S (mean of 2) 21.96, insol. 0.13; sum 99.62%. This corresponds closely to $4PbS \cdot FeS \cdot 3Sb_2S_3$, the accepted formula of jamesonite. However, the *x*-ray powder pattern is distinctly different from that of jamesonite. Occurs at the Herzsa mine, Kisbanya (=Chiuzbaia, Roumania), associated with and apparently later than sphalerite, galena, and pyrrhotite, and a little chalcopyrite. Small tetrahedra of tetrahedrite and needles of an unidentified mineral are later than the parajamesonite.

Michael Fleischer

Jujuyite

Federico Ahlfeld, An unusual antimony deposit in Argentina: *Econ. Geol.*, **43,** 598–602 (1948).

The name jujuyite (presumably pronounced hoo-hooey-ite, M.F.) is given to an iron antimonate. "It forms compact or earthy masses, rather pure or mixed with opal, chalcedony, and remnants of effusive rock. At first it was believed to be limonite. It shows a conchoidal fracture and has a dark-brown violet color. The specific gravity of a selected sample was determined to be 4.15 and the density 4.5." (Should the word density be hardness? M.F.) "Polished sections reveal a colloid structure. It is microcrystalline, with a weak anisotropism. A sample, carefully selected under the microscope, was analyzed in the laboratory of the Direccion General de Minas y Geologia, Buenos Aires, and gave:

Fe_2O_3 65.20, MnO 0.02, Sb_2O_5 18.59, SiO 11.70, H_2O 3.40, H_2O (105°) 0.77; Total 99.68%. No mineral of similar composition is known to the author. I would not venture to suggest a formula because some silica is present as a mechanical mixture in the form of chalcedony . . . ."

"Earthy yellow antimony oxide, probably cervantite" is also present. A sample of jujuyite from another vein is black with a glassy luster. Its specific gravity is 4.7 and a selected sample gave 21.63% Sb(=28.8% Sb_2O_5).

Juyuyite occurs as small veins in dacite lavas near Doncellas, 50 km. S. W. of Abra Pampa, province of Jujuy, northwestern Argentina.

Discussion: The data are clearly inadequate and a new name should not have been used until this heterogeneous variable material had been investigated more fully. The analyses show Sb_2O_5 contents much lower than those of the known iron antimonates flajolotite and tripuhyite, but these might be present admixed with iron oxides.

M.F.

Walker Mineralogical Club Prize

The Walker Mineralogical Club of the University of Toronto again offers a Prize ($100) for the best scientific paper on pure or applied mineralogy (including crystallography and petrology) submitted to the Club by a graduate student at any university or similar institution. Papers must be received *not later than May 31, 1949.* For further information write Walter Tovell, Secretary, 100 Queen's Park, Toronto, Canada.

The Spring Meeting of the Society for Experimental Stress Analysis will be held at Hotel Statler, Detroit, Michigan, on May 19, 20, 21, 1949. Inquiries should be addressed to the Society for Experimental Stress Analysis, P.O. Box 168, Cambridge 39, Massachusetts.

Handbook of Uranium Minerals by Jack De Ment and H. C. Dake has now appeared in a revised and enlarged second edition. The quick exhaustion of the first edition (see review in Am. Mineral., **32,** 698) indicates the popularity and interest in this timely pamphlet. Considerable new material has been added and many typographical errors of the first edition have been eliminated. It is designed primarily for the prospector, collector, student, and non-specialist, and should prove helpful to anyone interested in radio active minerals. Published by the Mineralogist Publishing Co., Portland 15, Oregon. Price $2.00.

During a recent trip East, Austin F. Rogers of Stanford University gave illustrated lectures on jade at the University of Virginia and at The Johns Hopkins University.

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SCHORTMANN'S MINERALS
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An Open Letter To Petrographers From Ward's

May we suggest that the confidence you have shown repeatedly in Ward's Mineralogy Department be extended now to our newly formed Scientific Instrument Division.

Not only do we offer Bausch & Lomb, Spencer and Leitz Polarizing Microscopes, but also a consultation service based on years of experience with the manufacture and design of these instruments. Dr. Kurt J. Heinicke, Manager of Ward's Scientific Instrument Division, has spent some sixteen years on the Bausch & Lomb and Leitz developmental staffs. His experience is at your disposal.

Knowing the present high replacement cost of polarizing microscopes makes it often necessary to use older instruments beyond their useful life. To this end, we have been contemplating the establishing of a repair and maintenance service designed to prolong their usefulness significantly. This contemplation is based on the fact that we now have on our staff, fine instrument makers trained in microscope building and repair. Yet, understandably we hesitate to offer their services without an expression from you on the points requiring preliminary consideration. For example, your comments are invited on the following:

1. The average time period that may be alloted for each microscope repair.
2. The desirability of establishing standard rates covering the recementing of polarizing prisms, refitting of stages, fine adjustment, centering nosepiece, objectives, eyepiece crosshair replacement, etc.

May we look forward to your comments?

Meanwhile, we hope you will call on us for your needs on new polarizing microscopes, universal stages, widefield microscopes of Bausch & Lomb, Spencer and Leitz manufacture. We offer two months delivery on the latter.

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